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THE EVOLUTION AND DEVELOPMENT OF THE QUANTUM THEORY

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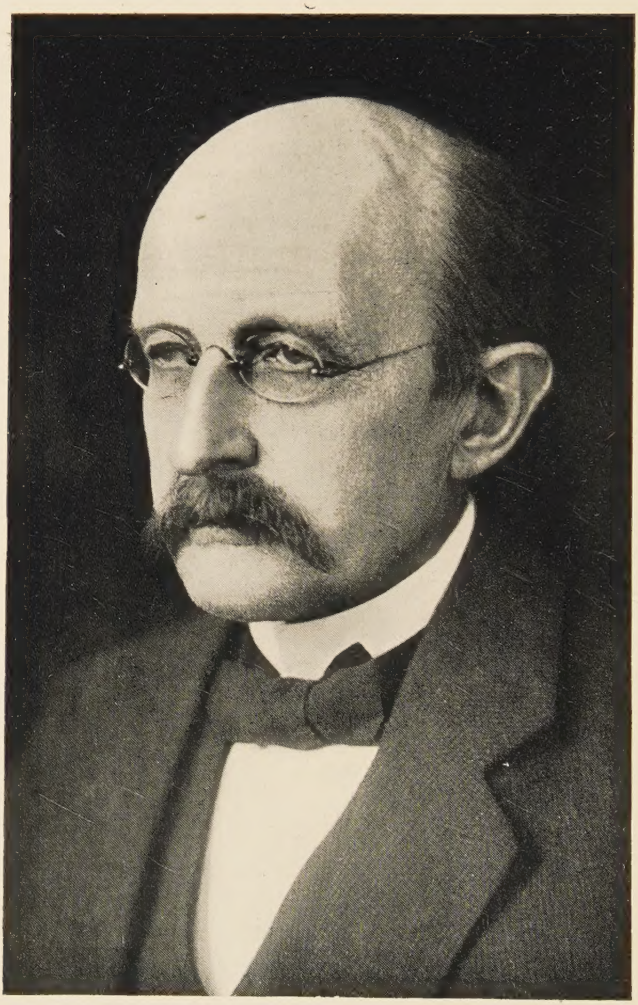

Professor Max Planck.

THE EVOLUTION AND DEVELOPMENT OF THE QUANTUM THEORY

BY

N. M. BLIGH, A.R.C.Sc., A.I.C.

WITH A FOREWORD BY

PROFESSOR MAX PLANCK

WITH FRONTISPIECE

NEW YORK

LONGMANS, GREEN & CO.

LONDON: EDWARD ARNOLD & CO.

1926

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Made and Printed in Great Britain by
Butler & Tanner Ltd., Frome and London

PREFACE

It is fairly safe to assert that the two outstanding features in the development of theoretical physics and allied science in the twentieth century have been the theories of Relativity and of Quanta. Their influence has been profound; they have gone far to generalise and unify our conception of natural phenomena, and have smoothed away and explained many difficulties and anomalies. The theory of Relativity, moreover, caught the popular imagination by very reason of its abstruse nature, inasmuch as it seemed to strike at the root of some of our most solidly founded notions. Partly no doubt as a result of its popularity an enormous number of treatises became available, graded to appeal to every type of reader, from the specialist's advanced textbooks to non-mathematical popular handbooks.

The Quantum Theory, on the other hand, is not in the least spectacular to the lay reader, and a fair knowledge of physics together with a balanced appreciation of its modern difficulties is necessary before the manifold and wonderful utility of the new theory becomes apparent. It is for this reason natural that no popular expositions are extant. The very nature and scope of the theory do not lend themselves to such treatment; but the remarkable fact remains that the general scientific reader finds himself without a concise handbook on the subject. In the English language there are isolated references in standard works on physics and a very limited number of detailed textbooks. The average reader or student has little time to wade through the latter, and separating the incidental from the essential, to obtain a view of the subject in its true perspective. In the present small volume a modest attempt is made to supply something intermediate between these two extremes of information. On being presented with a finished theory a natural curiosity is aroused as to how such a theory was evolved and built up. In these pages the rise of the theory is traced as far as possible in historical sequence, a mathematical deduction of each important law, bearing on the subject, is given as it arises; the difficulties encountered are indicated together with the means by which they were overcome. A special aim has been to follow an ordered and

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logical sequence, which seemed far preferable to consigning parts of the mathematical reasoning to appendices or footnotes. At the same time it should be easy for any reader, so inclined, to make an initial study of the descriptive matter only. The second part of the book deals with the more important applications of Quantum principles to general problems of physics. The author is well aware that only a limited number of these have been touched on ; to attempt mention of every sphere of application would have defeated the object of the book. The reader interested in such must be referred to the larger treatises. Very recently a fresh impetus has been given to the whole subject by the system of Quantum mechanics devised by Heisenberg ; and we are probably nearer to an understanding of fundamental principles than was until lately supposed. At the moment however a survey of the new developments would be premature in these pages.

The author's sincere thanks are due to Professor Planck for his kindness in writing a foreword and for his excellent photographic frontispiece, as well as for his encouragement and interest in the work. He is indebted to Dr. E. H. Tripp for his kind assistance, and to Dr. M. A. Whiteley, O.B.E., for the ready loan of a scarce book.

N. M. B.

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FOREWORD

By M. Planck, Ph.D., *Professor of Theoretical Physics in the University of Berlin.*

I willingly take advantage, in response to the desire expressed by the author of this work on the development of the Quantum Theory, of the opportunity to contribute a few prefatory remarks. Although I am well aware that the scientific value of the work cannot be enhanced by such an introduction, it enables me to direct attention to the great importance of the subject matter to all branches of physics. It may, indeed, be said without exaggeration that the concept of quanta is as much in the forefront to-day as it ever was, because it is even prepared to conquer such fields as that of pure mechanics, the theory of which has been generally regarded as definitely settled, everywhere substituting difference laws for differential laws. On the other hand, the difficulties encountered in fitting the quantum hypothesis into the system of theoretical physics have certainly proved to be much more formidable than one was originally inclined to assume; and this is especially true of the laws of propagation of radiant energy in free space. There can, however, be no doubt that these difficulties will be overcome as our knowledge increases and as modern mathematical methods come to our aid. The picture of the physical universe will then regain the complete unity of classical physics, but in form it will be more finished.

MAX PLANCK.

Berlin,
March, 1926.

PART I

THE EVOLUTION OF THE QUANTUM THEORY

I

GENERAL INTRODUCTION TO THE PROBLEMS OF RADIATION

The outstanding feature of theoretical physics in the present century is undoubtedly the rise of the theory of Relativity and the Quantum theory. At the commencement of the century Lord Kelvin spoke of two clouds obscuring the beauty and clearness of the dynamical theory of light and heat; the clouds being in fact the theories of Relativity and Quanta, which have grown to completely overshadow the older theory. Up to the end of the nineteenth century Newtonian mechanics, or the system of mechanics developed from the work of Newton, had been accepted as of universal application, inasmuch as it was found that practically all natural phenomena to which they were applied were capable of satisfactory treatment by their means, and in apparent conformity with them. Following the gradual perfecting of exact measurements in various spheres of science it has come to be realized that many previously accepted laws were merely close approximations to the truth.

As an illustration it may be mentioned that the atomic weights of the chemical elements were regarded as fundamental, until accumulated evidence led to the conclusion that not the atomic weights but the atomic numbers, a conception intimately related to the internal structure of the atom, were actually fundamental, and, except for certain outstanding instances, were roughly proportional to the atomic weights. The latter as established by chemical means satisfactorily interpret ordinary chemical phenomena, but on descending to the more minute measure-

ments associated with atomic structure, differences arise which do not accord exactly with atomic weight values. In other words, atomic weights are quite satisfactory for dealing with substances in quantity.

Again, in the realm of astronomical physics, the theory of Relativity has largely removed difficulties which can be traced to the enormous difference between the velocities of bodies under our direct control and the almost inconceivably great velocity of light. Exact investigations of astronomical phenomena showed that when certain considerations involving the velocity of light are introduced Newtonian dynamics are only approximately applicable, and require to be modified by a more exact mathematical treatment in accordance with the theory of Relativity.

The Quantum theory itself had its origin in the branch of physics dealing with radiation. The process of radiation had always been regarded as perfectly continuous, and on the basis of classical mechanics laws of radiation were deduced. Elaborate and exact practical measurements, however, showed that such laws were applicable only particularly and not generally. Accumulated evidence finally led to the view that absorption and emission of radiation was not a perfectly continuous process, but took place in individual units or quanta ; in other words a discontinuity had established itself which did not admit of mathematical explanation on classical dynamics. This discontinuity is in turn intimately associated with the discontinuity of electricity itself, i.e. as existing as electrons and protons, and the part played by these units in atomic structure. It should be emphasized that classical mechanics give a perfectly satisfactory method of treatment for matter in bulk and needs amendment only in the specialized regions indicated.

The Quantum theory in its rapid and successful development has found its way into practically every branch of physics : the question of specific heats, the propagation of light, X-rays, and atomic structure, to mention only a few ; in fact, into all considerations involving the relationship of energy to matter.

Radiation of heat, in contrast to conduction, is quite independent of the temperature of the medium through which it passes. In illustration of this there is the well-known fact that radiant heat from the sun, falling on an object in a cold atmosphere, can warm that object independently of the temperature of the surrounding atmosphere; similarly the radiant heat from the filament of an evacuated electric lamp causes a sensation of warmth in the neighbourhood of the bulb, while the glass of the

bulb remains, for the time being, cold. According to the kinetic theory of matter, the particles composing a solid, being in a state of rapid vibration, transmit to the surrounding space radiant energy in the form of waves, which according to Maxwell's electromagnetic theory are identical with electromagnetic waves, and differ only from visible light in the matter of wave-length. As regards physical properties they are propagated with the velocity of light, are identical with light waves of the same wave-length, and admit of the laws of experimental optics being applied to them.

The vibrating particles or radiators may be either the atoms or electrons composing the substance emitting radiation, and the waves produced must be of the same periodic frequency as that of the vibrating particles. If these particles all possessed the same period, the radiation emitted would be of a definite wave-length, and constitute light of a definite colour. Generally, however, the vibration periods of the particles vary over a large range, so that the emitted radiation actually covers a wide range of wave-lengths constituting a spectrum. Obviously the emission of radiation involves a loss of energy of the vibrating particles, which might be expected finally to become motionless, and emission of radiation to cease. The supply of energy may be maintained in two ways; firstly by chemical change or intramolecular changes such as combustion or incandescence, which gives rise to the type of radiation known as luminescence, or secondly by the temperature of the body itself being maintained at some definite high level. We are here concerned only with the latter way, in which the temperature is maintained by purely physical means, giving rise to temperature radiation. In this way the kinetic energy of the particles continues to have a high value and the radiators are thus kept in vibration. A body at ordinary room temperature, for instance, arrives at a temperature equilibrium with its surroundings, and consequently absorbs just as much radiation as it emits. When its temperature is artificially raised the kinetic energy of the particles increases, the frequency rises and hence also the frequency of the emitted radiation. Since for all wave motion the product of frequency and corresponding wave-length is equal to the velocity of wave propagation, the wave-length decreases with rise of temperature. Now just as the frequencies of the vibrating particles at any particular temperature vary over a large range, i.e. the majority vibrate at some rate characteristic of the temperature, but of the remainder a small number will have frequencies down to a very small value, and others up to a value

much above the average, so the frequencies of the emitted radiation will vary over a corresponding range. The maximum energy of the radiation may however be expected to correspond with the average vibration frequency of the radiators, and this maximum will vary with the temperature of the source of radiation. This important point will be considered more fully in connection with Wien's displacement law.

Considering now a source of radiation, the temperature of the source being gradually raised, the emitted radiation will first be recognizable as heat waves of relatively low frequency and long wave-length ; as the temperature of the source rises, waves of higher frequency are emitted until at about 525° C. visible light waves first permit of the source exhibiting a visible glow. (It will be seen later that this particular temperature of initial visible glow, first recognized by Draper, is, as a consequence of Kirchhoff's law, the same for all bodies.) The lower wave-lengths continue to be radiated in diminishing degree, while at a white heat a range of waves covering the visible light spectrum are in addition being emitted. It is therefore clear that at any moment the total radiation emitted is composed of a varying range of wave-lengths.

Heat is known to be a form of energy, hence the body under consideration is radiating energy to the ether of space, and the amount of energy radiated per second by one square centimetre of the body is known as the emissive power of the body.

Black-body Radiation.—Since the radiation travels at a definite speed, there must be, at any instant, energy of radiation in the ether itself. (It will not be necessary to discuss here the very controversial question as to the existence and nature of the ether.) It is noticeable that masses of different substances in a uniformly glowing red-hot fire lose their distinctive appearance and outline and present a uniform glow, hence their emissivity must be equal ; also for maintenance of constant temperature they must be receiving quantities of heat equal to that emitted. This leads us to the conception of a " black body " or full radiator, of immense importance in the theory of radiation. The uniformly glowing fire may be regarded as being replaced theoretically by a closed hollow sphere, prevented from exchanging heat with its surroundings, and interiorly fulfilling the conditions of a black body. For experimental purposes a minute aperture is necessary in order to examine the radiation from the interior by means of a radiometer outside, and results indicate that in such an enclosure, radiation is propagated in all directions, depending only on the temperature

of the enclosure and independent of the nature of the interior matter. A true black body emits and absorbs radiation of all wave-lengths and reflects none ; actually it need not look black, e.g. the interior of the fire exhibited a uniform reddish glow, but practically a lamp-black surface is found to approximate with the greatest degree of exactness to a true black body.

Kirchhoff's Law.—The considerations above are summarized in Kirchhoff's [1] Law of Cavity Radiation, formulated in 1859, and stating :—In an enclosure surrounded on all sides by reflecting walls, externally protected from exchanging heat with its surroundings, and evacuated, the condition of black radiation is automatically set up, if all the emitting and absorbing bodies at the walls or in the enclosure are at the same temperature.

From a consideration of an enclosure satisfying the above conditions some fundamental relations can be deduced.

Let $d\tau$ be a small volume element of a particle in the enclosure emitting black radiation at temperature T, and let $d\Omega$ be a solid angle having as vertex the point $d\tau$ and formed by the intersection of a sphere surrounding $d\tau$ as centre, and a cone drawn from $d\tau$. Also let ν be the frequency of a certain radiation emitted from $d\tau$ and $d\nu$ a small interval of frequencies lying between ν and $\nu + d\nu$. Since the medium is isotropic the emitted rays will be unpolarized and every ray will have twice the intensity of one of its plane-polarized constituents. Then the total energy in a range of frequencies $d\nu$ emitted in time dt in the direction of the conical element $d\Omega$ by a volume element $d\tau$ will be denoted by $E\nu$ (the emissivity of the particle for frequency ν), hence

$$E_\nu = dtd\tau d\Omega d\nu 2e_\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 1$$

where e_ν is the coefficient of emission of the body for frequency ν.

It will subsequently be shown that for a black body e_ν is just equal to the intensity of the radiant energy of the body, denoted by K_ν, hence we can write

$$E_\nu = dtd\tau d\Omega d\nu 2K_\nu . \quad . \quad . \quad . \quad . \quad . \quad 2$$

For the total energy from a volume element $d\tau$ integrate over all directions and for all frequencies. We have, for all conical elements, $\int d\Omega = 4\pi$,

hence $$E = dtd\tau 8\pi \int_0^\infty K_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad 3$$

Let K be the intensity of the radiated energy and K_ν and K_ν'

[1] *Sitzungsber. K. Akad. Wiss. Berlin*, 1859, 216; *Pogg. Ann.* 1860, **109**, 275; *Gesammelte Abhandlungen*, Leipzig, T. A. Barth, 1882, 573.

the intensities of the two plane-polarized components of a ray of frequency ν,

then $$K = \int_0^\infty (K_\nu + K_\nu')d\nu \quad . \quad . \quad . \quad . \quad . \quad 4$$

For unpolarized rays $K_\nu = K_\nu'$, hence we have

$$K = 2\int_0^\infty K_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 5$$

For the radiant energy of a narrow range of wave-length $d\lambda$ corresponding to frequency $d\nu$ we can write $E_\lambda d\lambda$, hence

$$E_\lambda d\lambda = K_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 6$$

If c is the velocity of propagation of radiation we have the general relation

$$\nu = \frac{c}{\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 7$$

Differentiating $$d\nu = -\frac{c}{\lambda^2}d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad 8$$

we can write 6 in the form

$$E_\lambda = K_\nu \frac{c}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad 9$$

Thus for a certain spectrum the maxima of E_λ and K_ν lie at different points of the spectrum.

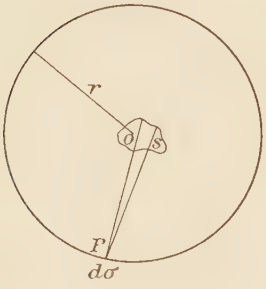

Fig. 1.

The space density of the radiation denoted by u will be defined as the total quantity of energy per volume element divided by the magnitude of the volume element.

Let v be a small element of volume in the medium, and round any point o in v a sphere of radius r is constructed, r being large compared with v (Fig. 1). $d\sigma$ is an infinitely small area element of the sphere, and s an element of length cut out by one of an infinite number of conical elements of a cone of rays from P to v; $\frac{f}{r^2}$ will be a solid angle of such a conical element where f is the area of cross-section normal to the axis of the cone at a distance r from P. The time required for radiation to pass through distance s will be $t = \frac{s}{c}$. The energy radiated through a certain element of area will be

$$dtd\sigma \cos\theta d\Omega K \quad . \quad . \quad . \quad . \quad . \quad . \quad 10$$

where θ is the angle made by the normal to $d\sigma$ with the direction of the radiation. Here $d\Omega = f, r^2$ and $\theta = o$, hence the energy is $td\sigma f\mathrm{K}, r^2 = \frac{fs}{r^2c}\mathrm{K}d\sigma$. This energy enters the conical element in v and spreads out into the volume fs. Summing up over all conical elements that start from $d\sigma$ and enter v, we have

$$\frac{\mathrm{K}d\sigma}{r^2c}\Sigma fs = \frac{\mathrm{K}d\sigma}{r^2c}v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 10a$$

This represents the entire energy of radiation in volume v so far as it is caused by radiation through the element $d\sigma$. For the total energy of radiation in v we must integrate over all elements $d\sigma$ contained in the surface of the sphere,

$$d\Omega = \frac{d\sigma}{r^2}.$$

From 10a the whole energy $= \frac{v}{c}\int \mathrm{K}d\Omega.$

For the volume density, dividing by v, we have

$$u = \frac{1}{c}\int \mathrm{K}d\Omega \quad . \quad . \quad . \quad . \quad . \quad . \quad 11$$

Hence for radiation uniform in all directions

$$u = \frac{4\pi\mathrm{K}}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 12$$

Also $$u = \int_0^\infty u_\nu d\nu$$

Then from 4 and 11 $u_\nu = \frac{1}{c}\int (\mathrm{K}_\nu + \mathrm{K}_\nu')d\Omega \quad . \quad . \quad . \quad 13$

Finally for unpolarized radiation uniformly distributed in all directions

$$u_\nu = \frac{8\pi}{c}\mathrm{K}_\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 14$$

Deductions Leading to Kirchhoff's Law. The contents of an impermeable enclosure will arrive at thermodynamic equilibrium for which the entropy will be a maximum. According to equation 3 the energy emitted in time dt by a volume element v will be

$$dtv8\pi\int_0^\infty e_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 15$$

To calculate the absorbed energy: The energy absorbed by a volume element v in time dt is found by considering the intensities of all rays passing through the element v and taking that fraction of each of these rays which is absorbed in v. According

to 10 the intensity of radiation for the conical element $d\sigma$ which cuts out a part fs from the volume v is $d\sigma f\mathrm{K}\ r^2$, and according to 5, by considering the different parts of the spectrum separately this will be

$$2d\sigma\frac{f}{r^2}\int_0^\infty \mathrm{K}_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 16$$

Hence the intensity of a monochromatic ray is

$$2d\sigma\frac{f}{r^2}\mathrm{K}_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 17$$

The amount of energy this ray absorbs in the distance s in time dt is

$$dta_\nu s2d\sigma\frac{f}{r^2}\mathrm{K}_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 18$$

where a_ν is the coefficient of absorption for frequency ν.

Thus the absorbed part of the energy of this small cone of rays, found by integrating over all frequencies, is

$$dt2d\sigma f\frac{s}{r^2}\int_0^\infty a_\nu \mathrm{K}_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad 19$$

$\Sigma fs = v$; also, summing all elements $d\sigma$ of a spherical surface of radius r, we have

$$\int\frac{d\sigma}{r^2} = 4\pi$$

Hence the total absorbed energy in time dt by the volume element v will be

$$dtv8\pi\int_0^\infty a_\iota \mathrm{K}_\iota d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 20$$

Equating emitted and absorbed energy,

$$\int_0^\infty e_\nu d\nu = \int_0^\infty a_\nu \mathrm{K}_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad 21$$

Hence

$$\mathrm{K}_\nu = \frac{e_\nu}{a_\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 22$$

Thus the ratio of emissive power to absorbing power for any body is a constant and is the same for all bodies, being independent of the nature of the body, and is just equal to the intensity of radiation for a black body under the same conditions; e_ν and a_ν themselves will be dependent on the temperature, frequency and nature of the body, but a black body is unique inasmuch as it is a perfect absorber for all radiation incident upon it, so that a_ν will be unity, hence $\mathrm{K}_\nu = e_\nu$ and for a black body K_ν will be a function of the temperature and frequency alone, i.e.

$$\mathrm{K}_\nu = f(\nu.\mathrm{T}) \quad . \quad . \quad . \quad . \quad . \quad . \quad 23$$

II

CONNECTION BETWEEN TEMPERATURE OF A BODY AND RATE OF ENERGY EMISSION

Dulong and Petit's Result. Many attempts had been made to find the connection between the temperature of a body and its rate of emitting radiant energy. According to Newton's law of cooling, the rate of cooling, i.e. the quantity of heat lost by a body in unit time, is proportional to the difference of temperature between the body and the surrounding medium. This law holds only for small differences of temperature between the body and the surrounding medium, and ordinarily is useful in calorimetric work. Dulong and Petit as a result of a series of experiments arrived at the conclusion that

$$v = k(a^t - a^{t'}) \quad . \quad . \quad . \quad . \quad . \quad . \quad 24$$

where v is the fall in temperature per second, i.e. velocity of cooling, t and t' are respectively the temperatures of the radiating body and of its surrounding medium, and k and a are constants depending on the nature and area of the surface of the radiating body. This law is quite empirical and holds only over a small temperature range ; thus both the above relations are applicable only to very limited experimental conditions.

Stefan's Empirical Result.—From Dulong and Petit's result, Stefan [1] in 1879 on purely empirical grounds arrived at an important relation bearing his name, and which states that the intensity of total radiation from a black body is proportional to the fourth power of its absolute temperature:

$$K = \sigma T^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 25$$

where σ = (Stefan's constant) $= 5{\cdot}32 \times 10^{-5}$ ergs per second per sq. cm.

or $= 1{\cdot}27 \times 10^{-12}$ calories per second per sq. cm.

It will be shown how a mathematical deduction of this law can be arrived at.

Maxwell, on the basis of his electromagnetic theory of light, deduced that a radiation pressure exists in the direction of

[1] Stefan, *Sitzungsber. K. Akad. Wiss. Wien*, 1879, **79**, 391.

propagation of electromagnetic waves, and this pressure was subsequently detected and measured experimentally.
It can be shown that

$$p = \frac{4\pi K}{3c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 26$$

where p is the radiation pressure, and c is the velocity of light.

We have already deduced the relation $u = \frac{4\pi K}{q}$,

hence

$$p = \frac{u}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 27$$

This simple relation is a special feature of the electromagnetic theory of light, and is independent of energy or thermodynamic considerations; it is not obtained from Newton's emission theory of light, although this theory is consistent with the energy principle.

The radiation pressure of Maxwell was used by Boltzmann [1] in 1884, in conjunction with the two laws of thermodynamics, to deduce the law previously enunciated by Stefan. Hence the relation is generally known as the Stefan-Boltzmann law.

The Stefan-Boltzmann Law.—We consider a perfectly evacuated hollow cylinder containing a tight piston free to move vertically without friction. The rigid bottom of the cylinder is a black body whose temperature T can be regulated from outside. The walls of the cylinder and the inner surface of the piston are totally reflecting. If the piston remains stationary, and at a temperature T, the radiation in the vacuum will, after a certain time, assume the characteristics of black radiation, uniform in all directions. The specific intensity of the radiation K, and the space density u, depend only on T and are independent of the volume V of the enclosure, and therefore of the position of the piston.

We have

$$U = Vu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 28$$

The work done by the system when the volume V of the cavity is increased by dV against the external forces of pressure is pdV. If dQ is the quantity of heat, which owing to the increased emission passes from the black bottom of the cavity, then the bottom loses heat dQ, and its internal energy is decreased by dQ. But since the sum of the energy of radiation and the energy of the material bodies is constant, we have

$$dU + pdV = dQ \quad . \quad . \quad . \quad . \quad . \quad 29$$

But from the second law of thermodynamics the cavity has a

[1] Boltzmann, *Wied. Annalen*, 1884, **22**, 291.

definite entropy,[1] and when heat $d\mathrm{Q}$ passes from the black base to the cavity, the entropy of the base decreased, the change being $-d\frac{\mathrm{Q}}{\mathrm{T}}$.

Let S be the entropy of the cavity containing the radiation. The processes described are states of equilibrium and are perfectly reversible, hence there is no increase of entropy, therefore

$$dS - d\frac{Q}{T} = 0$$

$$dQ = dU + pdV$$

$$dS = d\frac{Q}{T}$$

$$\therefore\ dS = \frac{dU + pdV}{T}$$

Since $p = \frac{u}{3}$ $\quad \therefore\ dS = \frac{dVu}{T} + \frac{udV}{3T}$

$$= \frac{udV + Vdu}{T} + \frac{1}{3}\cdot\frac{udV}{T}$$

$$= \frac{4}{3}\frac{udV}{T} + \frac{Vdu}{T}$$

$$= \frac{4}{3}\frac{udV}{T} + \frac{V}{T}\frac{du}{dT}dT$$

Since dS must be a complete differential

$$\frac{\partial S}{\partial T} = \frac{V}{T}\frac{du}{dt} \qquad \frac{\partial S}{\partial V} = \frac{4}{3}\frac{u}{T}$$

whence

$$\frac{4}{3}\frac{d}{dT}\left(\frac{u}{T}\right) = \frac{1}{T}\frac{du}{dt}$$

i.e.

$$\frac{4}{3}\left\{\frac{T\frac{du}{dT} - u\frac{dT}{dT}}{T^2}\right\} = \frac{1}{T}\frac{du}{dt}$$

$$\frac{4}{3}\left(\frac{1}{T}\frac{du}{dT} - \frac{u}{T^2}\right) = \frac{1}{T}\frac{du}{dT}$$

$$\frac{1}{3}\cdot\frac{1}{T}\frac{du}{dT} = \frac{4}{3}\frac{u}{T^2}$$

$$\frac{du}{dT} = \frac{4u}{T}$$

$$u = \sigma T^4 \quad . \quad . \quad . \quad . \quad . \quad 30$$

[1] See note on p. 42.

The above law, however, does not give us the energy density of the radiation corresponding to a definite frequency and temperature. We have considered how the heat radiation emitted from a hot body consists of a large range of wave-lengths constituting a spectrum, and the intensity of radiation throughout this spectrum is by no means equally divided. Thus when a body is first heated, the energy of emitted radiation must be concentrated mainly in the spectral region of dark heat rays, since any waves falling within the spectrum of visible light are present to such a minute extent as to be inappreciable to the eye. In formulating a general law of radiation the difficult problem has to be solved as to the distribution of the total energy radiated by a body among the individual grades of the spectrum at particular temperatures. There must be some definite small interval of wave-lengths over which the energy of radiation is greatest. Wien,[1] by reasoning on thermodynamic grounds, arrived at the conclusion that the energy density between a wave-length λ and $\lambda + \delta\lambda$ is a function of the wave-length and temperature alone, i.e. it takes the form $f(\lambda T)d\lambda$. If we find the wave-length corresponding to a maximum energy density, then $\frac{df}{d\lambda} = 0$ and this gives a certain value of λ which we will call λ_m. Wien showed that $\lambda_m T$ is a universal constant called Wien's constant, and also arrived at his so-called displacement law which, however, still contains an undetermined function. The derivation and significance of this law and the important conclusions to be drawn from it will now be considered in some detail.

Wien's Displacement Law.—We have now to determine u_ν and K_ν for black radiation in vacuo and hence in any medium as a function of the frequency ν and the temperature T, or to find the distribution of energy in the normal spectrum for any arbitrary temperature. Mathematically expressed,

$$K_\nu = f(\nu T) \quad . \quad . \quad . \quad . \quad . \quad . \quad 31$$

The law to be obtained, and formulated by Wien in 1894, is based on the theorem that if the black radiation contained in a perfectly evacuated cavity with totally reflecting walls is compressed or expanded adiabatically, that is with no transfer of heat to or from the cavity during the process, then the radiation always retains the character of black radiation.

In this compression work is done against the pressure of radiation, and this work must be changed into radiant energy

[1] Wien, *Sitzungsber. K. Akad. Wiss. Berlin*, 1893, 55; *Wied. Annalen*, 1894, **52**, 132.

and thus go to increase the intensity of the reflected ray. Account has to be taken of the fact that the waves reflected from the steadily advancing piston will undergo a change in accordance with Doppler's principle. Wien deduced that the wave-length of each constituent of the radiation would be shortened in proportion to the rise of temperature produced by the compression so that λT will be constant, and the energy $E_\lambda d\lambda$ in the range $\delta\lambda$ in other respects changes as a function of T alone. It can be shown that the change in wave-length will be

$$\delta\lambda = \frac{2\lambda v \cos\theta}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 32$$

where v is the velocity of the moving reflector.

We have seen from 10 that the energy emitted in time dt from a surface element $d\sigma$ at an angle θ with the direction of the radiation is

$$dtd\sigma \cos\theta d\Omega \mathrm{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 33$$

Substituting $d\Omega = 2\pi \sin\theta d\theta$, the above equation becomes

$$2\pi dtd\sigma \cos\theta \sin\theta d\theta \mathrm{K} \quad . \quad . \quad . \quad . \quad . \quad . \quad 34$$

If V is the volume of the enclosure, then from 12 the whole energy for which the wave-length lies between λ and $\lambda + \delta\lambda$ is

$$\frac{4\pi \mathrm{KV}}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 35$$

then the fraction of this energy which undergoes change of wave-length in time dt will be obtained by dividing 34 by 35, i.e.

$$\frac{cdtd\sigma \cos\theta \sin\theta d\theta}{2\mathrm{V}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 36$$

Multiplying by 32 the average change of wave-length will therefore be

$$\frac{\lambda v dtd\sigma \cos^2\theta \sin\theta d\theta}{\mathrm{V}} \quad . \quad . \quad . \quad . \quad . \quad . \quad 37$$

If $d\mathrm{V}$ is the total change of volume

$$d\mathrm{V} = dt \int v d\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 38$$

then for every element of surface and every angle of incidence the average change of wave-length will be

$$d\lambda = \lambda \frac{d\mathrm{V}}{\mathrm{V}} \int_0^{\frac{\pi}{2}} \sin\theta \cos^2\theta d\theta$$

$$= \tfrac{1}{3}\lambda \frac{d\mathrm{V}}{\mathrm{V}}$$

i.e. $$\frac{d\lambda}{\lambda} = \tfrac{1}{3}\frac{d\mathrm{V}}{\mathrm{V}}$$

i.e. $$\lambda \mathrm{V}^{-\frac{1}{3}} = \text{a constant.}$$

If we denote original values by λ_0 and V_0 and final values by λ and V we have

$$\frac{\lambda^3}{\lambda_0^3} = \frac{V}{V_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 39$$

To find the change in energy density u we observe that the loss of energy is equal to the work done, or since $U = Vu$

$$d(Vu) = -pdV = -\tfrac{1}{3}udV$$

whence $$Vdu + \frac{4}{3}udV = 0.$$

Integrating, $$\frac{u}{u_0} = \left(\frac{V_0}{V}\right)^{\frac{1}{3}} = \left(\frac{\lambda_0}{\lambda}\right)^4$$

But by Stefan's Law $$\frac{u}{u_0} = \frac{T^4}{T_0^4}$$

hence $$\frac{T}{T_0} = \frac{\lambda_0}{\lambda}$$

i.e. $$\lambda T = \text{a constant} \quad . \quad . \quad . \quad . \quad 40$$

The full expression for Wien's displacement law is now required. The form of the law is suggested by the following considerations.

In the adiabatic compression each constituent alters so that λT remains constant and the energy $E_\lambda d\lambda$ in the range $d\lambda$ in other respects changes as a function of T alone, i.e. $E_\lambda d\lambda$ must be of the form $F(T)f(\lambda T)d\lambda$. But for each temperature $\int_0^\infty E_\lambda d\lambda = E$ and so varies as T^4 according to Stefan's Law,

i.e. $$T^{-1}F(T)\int_\lambda^\infty f(\lambda T)d(\lambda T) \propto T^4$$

i.e. $$T^{-1}F(T) \propto T^4$$

hence $E_\lambda d\lambda$ is of the form $AT^5 f(\lambda T)d\lambda$, or since λ varies inversely as T we have $E_\lambda d\lambda = A\lambda^{-5}f(\lambda T)d\lambda$ where A is a constant.

The following is an outline of the method depending on thermodynamic considerations by which complete expressions of the law can be obtained, using the previously defined conception of black radiation in an enclosure.

Consider the radiation at a time t in a definite infinitely small interval of frequencies from ν to $\nu + \delta\nu$. At time t the total radiant energy will be $Vud\nu$, and at time $t + \delta t$ it will be $(Vu + \delta\overline{Vu})d\nu$, hence the change to be calculated will be the difference between these two, i.e. $\delta(Vu)d\nu$. Since equilibrium

exists we will calculate the radiant energy entering and leaving the interval of frequencies in the interval of time δt, and equate these two.

The energy leaving the interval in the time δt will be $2\pi f(\mathrm{K}_\nu d\nu)\delta t$. It can be shown that the energy entering can be represented by the expression $2\pi f\left(\mathrm{K}_\nu - \frac{4}{3}\frac{\nu v}{c}\frac{\partial \mathrm{K}}{\partial \nu}\right)\delta\nu\delta t$.

The difference between the latter equations will equal $\delta(\mathrm{V}u)d\nu$, hence

$$-\frac{8\pi}{3}f\frac{\nu v}{c}\frac{\partial \mathrm{K}}{\partial \nu}\delta t = \delta(\mathrm{V}u) \quad . \quad . \quad . \quad . \quad . \quad 41$$

From 14

$$\tfrac{1}{3}f\nu v\frac{\partial u}{\partial \nu}\delta t = \delta(\mathrm{V}u) \quad . \quad . \quad . \quad . \quad . \quad 42$$

Since $fv\delta t$ represents the decrease in the volume V, we have

$$\tfrac{1}{3}\nu\frac{\partial u}{\partial \nu}\delta \mathrm{V} = \delta(\mathrm{V}u) = u\delta \mathrm{V} + \mathrm{V}\delta u$$

Hence

$$\delta u = \left(\frac{\nu}{3}\frac{\partial u}{\partial \nu} - u\right)\frac{\delta \mathrm{V}}{\mathrm{V}} \quad . \quad . \quad . \quad . \quad . \quad 43$$

Introducing volume V, which depends only on t as the second variable, we have

$$\mathrm{V}\frac{\partial u}{\partial \mathrm{V}} - \frac{\nu}{3}\frac{\partial u}{\partial \nu} - u \quad . \quad . \quad . \quad . \quad . \quad 44$$

The general integral gives us $u = \frac{1}{\mathrm{V}}\phi(\nu^3\mathrm{V})$ 45

Substituting $\nu^3\mathrm{V}\phi(\nu^3\mathrm{V})$ for $\phi(\nu^3\mathrm{V})$, we have $u = \nu^3\phi(\nu^3\mathrm{V})$ . . 46

From the laws of thermodynamics we have the relation

$$d\mathrm{S} = \frac{d\mathrm{U} + p d\mathrm{V}}{\mathrm{T}}$$

On integration

$$\mathrm{S} = \frac{4}{3}\sigma \mathrm{T}^3\mathrm{V}$$

For a reversible adiabatic change the entropy S of a system remains constant,

hence

$$\mathrm{T}^3\mathrm{V} = \text{a constant.}$$

Then from 46

$$u = \nu^3\phi\left(\frac{\nu^3}{\mathrm{T}^3}\right) = \nu^3\phi\left(\frac{\mathrm{T}}{\nu}\right) \quad . \quad . \quad . \quad . \quad . \quad 47$$

From 14 we have

$$\mathrm{K}_\nu \propto u_\nu c$$

and from 22

$$c^2\mathrm{K}_\nu = c^2\frac{e_\nu}{a_\nu}$$

Therefore $u_\nu c^3$ is a function of T and ν.

Hence from 47 $$u = \frac{\nu^3}{c^3} f\left(\frac{\mathrm{T}}{\nu}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad 48$$

From 14 $$\mathrm{K}_\nu = \frac{\nu^3}{c^2} f\left(\frac{\mathrm{T}}{\nu}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad 49$$

And finally from 9 $$\mathrm{E}_\lambda = \frac{c^2}{\lambda^5} f\left(\frac{\lambda \mathrm{T}}{c}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad 50$$

Expressions 49 and 50 above are forms of Wien's Displacement Law.

Analysis of Wien's Results.—The law just deduced shows us that the energy radiated between a small interval of wave-lengths from λ to $\lambda + \delta\lambda$ is a function of $(\lambda \mathrm{T})$ and in general takes the form $\lambda^{-5} f(\lambda \mathrm{T})$, which, since λ^{-1} is proportional to T, can be written $\mathrm{T}^5 f(\lambda \mathrm{T})$.

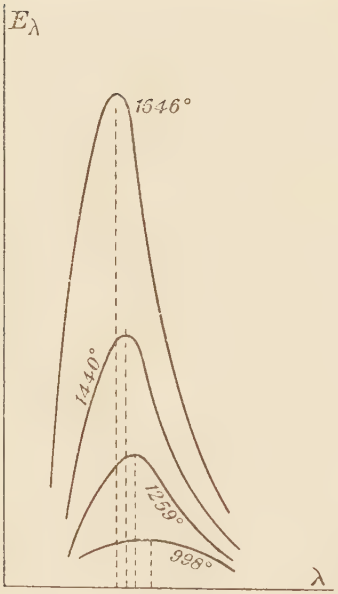

Fig. 2.

The curve (Fig. 2) is the general result of plotting intensities of radiation E_λ against wave-length λ for various specified temperatures. It will be noticed that the curves reach maxima corresponding to certain wave-lengths.

From Wien's deductions we have seen that $\lambda_{\max} \mathrm{T}$ is a constant[1] (Wien's constant), where $\lambda_{\max}$ is the wave-length emitting maximum energy. Obviously as T increases λ must decrease, thus for increasing temperatures the position of the maximum energy wave-length is *displaced* towards the shorter wave-lengths. We have seen above that

$$\mathrm{E}'_{\max\,\lambda} d\lambda = \mathrm{T}^5 f(\lambda \mathrm{T})$$

[1] Wien's constant = 0·294 cm. deg.: Lummer and Pringsheim, *Verh. deutsch. physikal. Ges.* 1899, **1**, 23 and 215.
0·292 cm. deg.: Paschen, *Drude's Ann.* 1901, **6**, 657.
0·291 cm. deg.: Coblentz, *Bull. Bur. Stand.* 1914, **10**, 1.

i.e. the energy radiated through a small range of wave-length $d\lambda$ at the maximum is proportional to T^5; thus the height of the curve is proportional to T^5;

i.e. for a maximum $$\frac{df}{d\lambda} = 0;$$

i.e. $$E_{\max \lambda}\, d\lambda \propto T^5.$$

According to Stefan's Law the *total* energy radiated for any particular temperature,

i.e. $$\int_0^\infty E_\lambda d\lambda,$$

is proportional to T^4, and is represented by the area under the curve above the x axis.

III

STATISTICAL MECHANICS

Wien's Law has been deduced on purely thermodynamic considerations, together with Maxwell's conception of radiation pressure. The next problem is to evaluate the undetermined function in the law. This was attacked by Wien himself in 1896 by a method based on Maxwell's law of the distribution of velocities among gas molecules. The deduction of this law depends on a principle known as statistical mechanics which furnishes a new and extremely useful means of dealing with radiation and the development of the subjects under review.

In the kinetic theory we base our calculations on the assumption that all the molecules in a particular portion of matter are identical in all respects. In the case, for instance, of velocity this obviously must be false ; we have however no means of selecting a single molecule or a specified small number of molecules and following and dealing with their actual velocities, energies or positions. Thus in practice a relatively very large number of molecules are considered as a whole, and calculations are made on the average velocity of this large number. In view of the extreme minuteness of the molecules this procedure is perfectly justified, and our results are simply average values. The introduction of statistics into mechanics is largely due to Maxwell and Boltzmann and consists essentially in applying the mathematical theory of probability to mechanics.[1] As opposed to the methods of the kinetic theory this does not mean that calculations are to be made of the precise energies, velocities, etc., of particular individual molecules, but that we are to investigate which are likely to be the most probable velocities, etc., of a mass of molecules. Considering such a mass there must obviously be a maximum and minimum value for the velocity of any particular molecule. For a gaseous mass we can, for instance, consider that as a result of collisions a molecule might for an infinitesimally small period of time be brought to rest ; on the other hand we can imagine the whole of the energy of the mass momentarily

[1] Meyer's *Kinetic Theory of Gases*, translated by Baynes ; Jeans' *Dynamical Theory of Gases* ; *Phil. Mag.* 1860 [iv], **19**, 19 ; **20**, 21 and 33 ; *Brit. Assoc. Rept.* 1859.

associated with a single molecule which would have a theoretically maximum velocity. Though these two extremes are not dynamically impossible, the probability of their occurrence is vanishingly small.

It is more reasonable to expect that the speeds of the molecules approximate to an average value, and the theory of probability proposes to investigate the most likely velocity out of all the theoretically possible values. The principle was used by Maxwell to investigate the distribution of velocities among the molecules of a gas, and leads to the view that certain speeds are more privileged than others, or that a certain speed exists towards which the actual velocities of the molecules approximate rather than towards any other speed. It will thus be seen that the results of statistical mechanics lead in a certain sense to an average result differing however very definitely from the purely mean average value of kinetic theory considerations where no account is taken of any question of actual probability.

In the same way, as regards actual place distribution, if we consider a gas occupying a certain definite volume, it is possible to conceive that at some instant the whole of the molecules should be concentrated in a space representing a small fraction of the total volume. The probability of this occurrence is extremely small ; in fact it can be calculated that the most probable state is that of uniform space distribution, and that the probability of this state being departed from is very small.

Algebraical Probability.[1] —According to the theory of probability stated algebraically, if an event can happen in a ways and fail in b ways and each of these ways is equally likely, then the chance of its occurring is $a/a + b$ and the chance of its failing is $b/a + b$. Certainty being represented by unity, the sum of the above two possibilities is unity, which therefore covers every circumstance. Hence the probability is represented by a fraction which cannot exceed unity.

Thermodynamic Probability.—According to the kinetic theory, the molecules of a gaseous system are moving about in a completely chaotic manner on account of their mutual collisions. Though under actual conditions no ordered arrangement is ever realized, we can however imagine a purely theoretical state in which at a given initial instant the molecules start from a perfectly ordered arrangement, and trace theoretically the subsequent development of conditions. By reason of collisions the molecules immediately tend towards a state of confusion as regards positions and velocities, confusion which must increase until

[1] Cp. e.g. Hall and Knight's *Higher Algebra.*

further disorder of molecular motion is impossible. In this state the system is in a state of kinetic equilibrium. If we designate the state of perfectly ordered arrangement as the standard state, and denote it by unity, then the ratio of the probability of the actual state or state of maximum chaos to the standard state is defined as the thermodynamic probability of the system. Since the chance of occurrence of the standard state is vanishingly small, the thermodynamic probability will in general be represented by an integer greater than unity. Its representation is therefore not the same as algebraical probability which cannot exceed unity.

It is here necessary for the further development of the above principle to explain more fully the state of a system or arrangement of the particles of a system and the method of applying probability considerations to the arrangements.

Suppose we have N objects to be distributed equally in each of n spaces. The distribution having been made, let the objects in each of the n spaces be so marked that they may be subsequently identified, e.g. let each object in the first space be marked 1, each in the second space marked 2, and so on. The whole of the objects are now collected, shaken together, and the distribution again made. Now in every space there will be still the same number of objects, but if N and n are sufficiently large, it is unlikely that any object which was originally in any particular space will be in the same space again ; for instance, it will be unlikely that any object numbered 50 as being in the fiftieth space originally will again be in the fiftieth space. We have by our second distribution produced a fresh "complexion." In considering the complexions formed we are solely concerned with the total number of objects in each space and not with their arrangement in the space. The probability of a chance occurrence of our particular distribution must be proportional to the number of complexions of which it is capable, since every complexion has an equal chance. This is proportional to the number of ways the N objects can be arranged in a row, i.e. $\lfloor N$. This however includes every possible arrangement of the n objects in each space, with which the complexion is not concerned, hence the probability required will be $\lfloor N / \lfloor n_1 \lfloor n_2 . \ . \ .$ A complexion is thus the number of ways in which a particular arrangement can be carried out, which is obviously not the same as the number of arrangements possible. Since any complexion is equally probable, i.e. each complexion possesses maximum probability, the number of possible complexions is identical with the thermodynamic probability of the system considered.

The laws of probability have been applied by Maxwell to determine the distribution of velocities among the molecules of a gas. Against his original proof objections have been urged which led Maxwell himself to amend it; since then a number of proofs have been advanced, all aiming at avoiding various unwarrantable assumptions.

Maxwell employed the assumption of molecular chaos according to which the molecules, regarded as hard elastic spheres, and having velocity components lying within any small specified limit, are at every instant distributed at random throughout the gas, independent of the position or velocity of other molecules, provided only that two molecules do not occupy the same space. Maxwell's proof considers the components of the velocity of a molecule in three rectangular directions using three velocity co-ordinates u, v and w. Its weakness is that it assumes the three velocity components to be independent.

It is of interest for our purpose to indicate how the considerations may be generalized. Just as we can have two co-ordinates in an imaginary space of two dimensions, so we can represent any four co-ordinates in an imaginary space of four dimensions. Similarly if a dynamical system is specified by any number n of co-ordinates we can represent these in a space of n co-ordinates. If we regard a gas as a single dynamical system, and represent its co-ordinates in a single imaginary space of the appropriate number of dimensions, then for N molecules each molecule will have six co-ordinates, three positional co-ordinates of its centre referred to three rectangular axes in the containing vessel and three components of the velocity of its centre resolved parallel to these three axes.

Maxwell's proof deals only with the average properties of all the systems represented in the generalized space, and gives no information as to the properties of any single system. An attempted modification is that instead of applying to an average taken over all the systems, it shall apply to the motion of one system averaged through a great length of time. The usual assumption made is that of continuity of path, i.e. that the system if left to itself will sooner or later pass through every phase which is consistent with the conservation of energy.[1] A modified proof of Maxwell's distribution law is given below.

Considering a gaseous system containing a very large number

[1] A full discussion of Maxwell's Law, subsequent proofs and generalization of proof will be found in Jeans' *Dynamical Theory of Gases*. See also Meyer's *Kinetic Theory of Gases*.

of molecules N, let δn be the number of molecules having velocities whose x components lie between u and $u + \delta u$.

To calculate the most probable distribution of groups containing δn molecules in the velocity intervals:

The probability of a certain distribution being the actual one is

$$\frac{\lfloor \underline{N}}{\Sigma \lfloor \underline{\delta n}}$$

therefore if w denotes the thermodynamic probability for the system

$$w = \frac{\lfloor \underline{N}}{\Sigma \lfloor \underline{\delta n}}$$

Hence $$\log w = \log \lfloor \underline{N} - \log \Sigma \lfloor \underline{\delta n}$$

For the most probable state this must be a maximum, i.e.

$$- \log \Sigma \lfloor \underline{\delta n} = 0.$$

By Stirling's theorem [1]

$$- \Sigma \delta n \log \delta n = 0.$$

we have to satisfy the conditions

$$\Sigma \delta n = 0$$

and $\Sigma \varepsilon \delta n = 0$ where ε = the energy of the system,

i.e. $\Sigma \frac{1}{2} m v^2 \delta n = 0.$

Multiply these equations by α and β respectively and add to previous equation,

i.e. $\Sigma \delta n [\log \delta n + \alpha + \beta v^2] = 0$

i.e. $\log \delta n = - (\alpha + \beta v^2)$

i.e. $\delta n = A e^{-\alpha} . e^{-\beta v^2} dv$ where A is a constant

$= A e^{-\gamma v^2} dv.$

Hence this fraction of the molecules present satisfies the conditions. Having regard to the total number of molecules

$$dn = N A e^{-\gamma v^2} dv.$$

The Principle of Equipartition of Energy.—This principle, associated with the names of Maxwell and Boltzmann, has been deduced on the basis of statistical mechanics, and figures largely in the evolution of the Quantum Theory. The principle states that in a system consisting of a large number of particles, the kinetic energy of the system is on the average equally distributed among the degrees of freedom of the particles. It will first be necessary to explain the term degree of freedom.

[1] See note, p. 51.

The number of degrees of freedom of a system may be defined as the number of independent quantities or co-ordinates which must be known to define fully the configuration and position of the system. We can regard a degree of freedom as a mode in which a body can be displaced, or a direction of motion; this obviously does not depend in any way on the forces which produce the motion, i.e. it is independent of the dynamics of the system.

The molecules of a gaseous system may possess three types of energy, each of which is a function of the temperature—Energy of Translation, Vibration, and Rotation—and such a type of energy may be kinetic alone, or partly kinetic and partly potential. It will be convenient to summarize the three types of energy in conjunction with degrees of freedom as follows:

1. *Energy of Translation.*—Motion along free paths; energy wholly kinetic. Three space co-ordinates, and hence three degrees of freedom.

2. *Energy of Vibration.*—Oscillation with respect to a fixed centre of gravity under the influence of a restoring force. One, two or three degrees of freedom. Energy potential and kinetic, in equal average amounts of each per vibration. For a monatomic gas, no atomic vibration is possible since there is no restoring force. For a diatomic gas there may be linear vibration of one atom with respect to another, in which case one degree of freedom; or circular vibration with respect to a centre of gravity and two degrees of freedom. For a triatomic molecule, probably a vibration of the atoms in pairs, hence three degrees of freedom.

3. *Energy of Rotation.*—Specific heat considerations indicate no energy of rotation in the case of a monatomic gas. For a diatomic molecule we have precessional vibration of the molecule as a whole, giving two degrees of freedom.

The total number of degrees of freedom of the molecules of a system will be the sum of the possible degrees for the type of molecule considered, in accordance with the above scheme.

For a monatomic solid, consistent with its solidity, free translation of the molecules is impossible. Hence there will be vibration of the atoms in three directions in space and hence three degrees of freedom.

A free point in space will have three degrees of freedom, i.e. the three co-ordinates of the point. A rigid body will have six degrees of freedom, i.e. the three co-ordinates of its centre of gravity, and three angles determining its orientation. Regarding an atom as a point, each atom will have three degrees of freedom.

From what has been said we conclude that a molecule of n atoms will have $3n$ degrees of freedom. If electrons are regarded as points the degrees of freedom for n electrons will be $3n$, and for a gas containing N molecules $3N$; and if each molecule has n degrees then the gas must have a total of nN degrees of freedom.

To deduce a quantitative statement of Maxwell's equipartition law in the case of a perfect gas we have the relation

$$PV = RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 51$$

also

$$P = \tfrac{1}{3}\varrho u^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 52$$

where ϱ is the density of the gas and u the root mean square velocity.

For one gram molecule $\varrho = \dfrac{M}{V}$ where M is the molecular weight and V the molecular volume.

Hence

$$PV = \tfrac{1}{3}Mu^2 = \tfrac{1}{3}Nmu^2$$

where N is the number of molecules per gram molecule (Avogadro's number) and m is the mass of one molecule.

For a single molecule the kinetic energy KE is $\frac{1}{2}mu^2$, hence for one gram molecule

$$KE = \tfrac{1}{2}Nmu^2$$

$$= \frac{3}{2}RT. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 53$$

A gas molecule has three degrees of freedom in respect of translation, hence the kinetic energy per degree of freedom is $\frac{1}{2}RT$.

To obtain the kinetic energy per degree of freedom of a single molecule, we divide by N, hence

$$KE = \tfrac{1}{2}\frac{R}{N}T$$

$$= \tfrac{1}{2}kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 54$$

where k is the gas constant per single molecule.

Maxwell's distribution law can be expressed in two ways. We have seen that

$$dn = NAe^{-\gamma u^2}du \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 55$$

where dn denotes the number of molecules out of a very large number N, whose X velocity components lie between small limits u and $u + du$.

Having regard to those whose Y and Z velocity components lie between v and $v + dv$ and w and $w + dw$ respectively, we arrive at the general expression

$$NA^3e^{-\gamma(u^2 + v^2 + w^2)}\,dudvdw \quad . \quad . \quad . \quad . \quad 56$$

In this way the expression corresponds to the normal law of errors which can be expressed

$$y = e^{-h^2x^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 57$$

where x denotes the error and y the probability of its occurrence. This law gives a symmetrical curve of the form shown in Fig. 3.

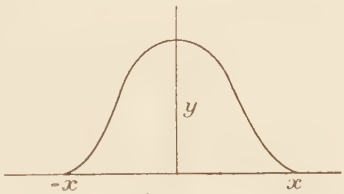

Fig. 3.

It will be seen that any of the particular components u, v, w in Maxwell's expression corresponds to x in the law of errors.

Maxwell's expression will be observed to involve the squares of velocities, and as the kinetic energy of a molecule depends on the squares of velocities we may pass to Maxwell's expression for the distribution of kinetic energy among the molecules of a gas.

Each molecule will have kinetic energy represented by

$$\tfrac{1}{2}m(u^2 + v^2 + w^2).$$

Hence for the distribution of kinetic energy we have the expression

$$\tfrac{1}{2}\mathrm{N}A^3m(u^2 + v^2 + w^2)e^{-\gamma(u^2 + v^2 + w^2)}dudvdw \quad . \quad . \quad 58$$

It can be shown that the constant γ has the form

$$\gamma = \frac{3}{2\bar{c}^2}$$

and

$$A = \sqrt{\frac{\gamma}{\pi}}$$

Hence the original expression 56 above takes the form

$$\mathrm{N}A^3e^{-\frac{3}{2\bar{c}^2}(u^2 + v^2 + w^2)}\,dudvdw \quad . \quad . \quad . \quad . \quad 59$$

or

$$\mathrm{N}\sqrt{\frac{27}{8\pi\bar{c}^6}}\,e^{-\frac{3}{2\bar{c}^2}(u^2 + v^2 + w^2)}\,dudvdw \quad . \quad . \quad . \quad 60$$

The term $\bar{c}$ denotes the root mean square velocity of a molecule; if v_1, v_2 . . . etc., are the molecular speeds at any instant, then

$$\bar{c}^2 = \frac{{v_1}^2 + {v_2}^2 + {v_3}^2 + \text{——}}{n}$$

where n is the number of molecules considered.

Whereas if c denotes simply the average velocity, then

$$c = \frac{v_1 + v_2 + v_3 + \text{——}}{n}$$

The relation between the two is given by

$$c = \frac{4}{\sqrt{6\pi}}\bar{c} = 0{\cdot}9213\bar{c}$$

If u, v and w are Cartesian co-ordinates in a three-dimensional space we may write

$$\omega^2 = u^2 + v^2 + w^2.$$

Then if we represent each molecule as a point in the velocity space $dudvdw$, the latter can be replaced by an element of volume $d\omega$. We can now express Maxwell's Law to represent the distribution of molecular velocities without any restriction as to direction of motion in the form

$$\mathrm{N}A^3 e^{-\frac{3\omega^2}{2\bar{c}^2}} d\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 61$$

This gives us the density of the velocity points round any point on a sphere of radius ω whose centre represents rest, and shows that as we recede from that point, the density of distribution of the points diminishes exponentially.

We can now formulate the second method of expressing Maxwell's Law. To find the number of molecules whose speeds, unrestricted as to direction, at any moment lie between the limits ω and $\omega + d\omega$ we must find the number of molecules lying between spherical surfaces of radius ω and $\omega + d\omega$. This volume is $4\pi\omega^2 dw$, hence the distribution law takes the form

$$4\pi\mathrm{N}A^3\omega^2 e^{-\frac{3\omega^2}{2\bar{c}^2}} d\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 62$$

This expression, it will be noticed, is not of the form of the law of errors, since 62 is of the form

$$x^2 e^{-x^2}.$$

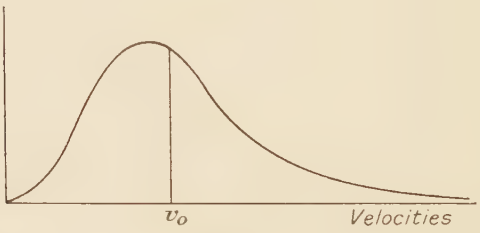

Fig. 4.

Representing the second method of expressing Maxwell's Law by a graph (Fig. 4) in which the abscissæ denote velocities, and ordinates denote fractions of the total number of molecules,

so that the height of the curve corresponding to any velocity represents the relative number of molecules having that velocity, it is seen that the curve is dissimilar to that of Fig. 3.

Starting from the origin, the curve rises to a maximum and then falls asymptotically to the x axis. Clearly the great majority of the molecules have velocities in the neighbourhood of the average value v_0, while a vanishingly small number have velocities approaching either zero or a very high value.

Finally we can express the distribution of kinetic energy among the molecules in a second form.

If E is the energy of motion of a molecule

then $$\mathrm{E} = \tfrac{1}{2}m\omega^2,$$

and if $\bar{\mathrm{E}}$ is the mean molecular kinetic energy

$$\bar{\mathrm{E}} = \tfrac{1}{2}m\bar{c}^2,$$

from 54 $$= \frac{3}{2}k\mathrm{T}$$

$$d\mathrm{E} = m\omega d\omega.$$

Then 62 takes the form

$$\mathrm{C}\mathrm{E}^{\frac{1}{2}}e^{-\frac{3\mathrm{E}}{2\bar{\mathrm{E}}}}d\mathrm{E} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 63$$

or from 54 $$\mathrm{C}_1\mathrm{E}^{\frac{1}{2}}e^{\frac{\mathrm{E}}{k\mathrm{T}}}d\mathrm{E} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 64$$

IV

WIEN'S LAW OF RADIATION

The extreme importance of the introduction of statistical mechanics into the study of radiation will be obvious since by its means through Maxwell's distribution law Wien [1] was first able in 1896 to formulate from his displacement law a definite law of radiation free from undetermined functions. As will subsequently be shown, this by no means exhausts the usefulness or importance of statistical mechanics as regards radiation.

In order to evaluate the function in the displacement law Wien applied Maxwell's distribution law to the molecules of a black body. He considered an enclosure containing a perfectly black body and assumed the molecules to be distributed in accordance with the distribution law; he also assumed that molecules having velocities lying within certain small limits at a certain time will emit radiation within certain small limits of frequency, and that the intensity of emission will be proportional to the number of molecules thus emitting. The validity of these latter assumptions is however to some extent open to question.

According to the displacement law E_λ is of the form $C\lambda^{-5}f(\lambda T)$ where C is a constant, and we have seen that from Maxwell's Law the number of molecules with velocities between v and $v + dv$ is of the form

$$\omega^2 e^{-\frac{3\omega^2}{2\bar{c}^2}}$$

Expressing ω as a function of λ and noting that $\bar{c}^2$ is proportional to T, we have for the number of molecules $c' f\lambda e^{-\frac{f\lambda}{T}} d\lambda$.

The energy will be proportional to this expression and to some other function of λ,

hence $$E = F\lambda e^{-\frac{f\lambda}{T}}$$

Then from our original expression

$$E = C\lambda^{-5} e^{-\frac{\beta}{\lambda T}}$$

[1] Wien, *Wied. Ann.* 1896, **58**, 662.

From our earlier results we can rewrite this

$$E_\lambda = a\frac{c^2}{\lambda^5}e^{-\frac{\beta}{\lambda T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 65$$

or

$$K_\nu = a\frac{\nu^3}{c^2}e^{-\frac{\beta\nu}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 66$$

where a and β are two constants.

In the following section will be considered how far this law is in agreement with the results of experimental observations.

Progress of Practical Research on Radiation. Up to the present we have considered theoretical researches and deductions on the problems of radiation, but concurrent with these a large amount of experimental research was conducted with the object of testing the various relations which had been proposed and making measurements with a view to calculating the relationships. It is now proposed to give some account of the work done in this direction. The experimental realization of black-body radiation was attempted by W. Wien and O. Lummer [1] on the basis of Kirchhoff's law of cavity radiation which has been already discussed. The outstanding research in the field of radiation is the most complete series of experiments conducted by O. Lummer and E. Pringsheim [2] at the Reichsanstalt, Charlottenburg, during the period 1897 to 1899. For realization of a black body these two investigators used a hollow copper sphere coated on the inside with lamp-black for a lower temperature range and an iron cylinder internally coated with platinum black for higher temperatures. Suitable means were adopted for maintaining the enclosures at definite temperatures, and the intensity of radiation emitted from the enclosure through a small aperture was compared at different temperatures by means of a bolometer. This instrument, invented by Langley, depends for its use on the change of electrical resistance with temperature of a fine platinum wire. The temperature of the fully radiating enclosure for a range between 200° C. and 600° C. was found by means of a high-pressure mercury thermometer and a thermo-couple, and for a higher range of temperatures by a thermo-couple. In this way they found that Stefan's fourth-power law was satisfactory for a whole range of experiments from — 190° C. to 2300° C. The value of Stefan's constant was found by Kurlbaum,[3] using

[1] *Wied. Ann.* 1895, **56**, 451.

[2] *Wied. Ann.* 1897, **63**, 395. *Verh. deutsch. physikal. Ges.* 1899, **1**, 22, 215; 1900, **2**, 163; *Drude's Ann.* 1900 [iv], **3**, 283; 1901 [iv], **4**, 225.

[3] *Wied. Ann.* 1898, **65**, 746.

an electrical method; Valentiner[1] used a similar method and employed temperatures from 440° C. to 1550° C. which he measured by means of a thermo-couple and nitrogen thermometer.

In order to test Wien's displacement law it was necessary to disperse the radiation; this was effected by placing a fluorite prism near the aperture and observing with a bolometer the intensity at different points of the spectrum. Results obtained in this way at various temperatures supply data for the construction of curves as in Fig. 2. The results of Lummer and Pringsheim largely confirmed the law, and a value for Wien's constant was obtained.[2] Experiments were also made to test Wien's radiation law, the above method being used by the same two experimenters,[3] and in later determinations the original fluorite prism was replaced by one of sylvine.[4]

Rubens and Nichols[5] found that quartz and fluorite prisms possessed the property of selective reflection for rays of certain wave-length, and that these rays could be isolated by four to six reflections. The net result was to show that the radiation law was obeyed only for high frequencies or short wave-lengths

or large values of $\frac{\beta\nu}{T}$, while for long wave-lengths systematic

discrepancies were detected. Paschen,[6] however, decided in favour of the law; but his work was conducted on visible rays, using a photometer instead of a bolometer. Since the visible rays are of relatively higher frequency for which Lummer and Pringsheim confirmed the law, Paschen's results can be understood.

Planck's Earlier Work on a Law of Radiation.—The next contribution towards the treatment of the radiation problem was due to Professor Max Planck of Berlin, by whose genius a satisfactory solution was ultimately obtained. It seemed necessary, in order to evaluate Wien's function, to select some body, the laws of emission and absorption of which were known, and to calculate the heat radiation when the exchange of energy was stationary, this according to Kirchhoff's theorem being

[1] *Ann. Physik,* 1910 [iv], **31,** 255; 1912 [iv], **39,** 489.
[2] Cf. note, p. 26
[3] *Verh. deutsch. physikal. Ges.* 1899, **1,** 34.
[4] *Ibid.* 1900, **2,** 163.
[5] *Wied. Ann.* 1897, **60,** 418.
[6] *Sitzungsber. K. Akad. Wiss. Berlin,* 1899, 405, 959.

independent of the nature of the body. Planck [1] considered a system of Hertzian oscillators,[2] or electromagnetic oscillators consisting of two poles of opposite and equal charges. If a large number of these oscillators are contained in an enclosure having reflecting walls they will exchange energy with one another by the absorption or emission of electromagnetic waves until a stationary state, or black radiation, is reached. Each vibrating oscillator will have a fixed natural frequency ν and, from an analogy with sound, will respond only to waves of radiation in the enclosure whose frequencies approximate to that of the resonators and will be unaffected by waves of other frequencies. Hence an oscillator exchanges energy with the radiation as a resonator, and as an emitter for waves of its own natural frequency, until a state of equilibrium is reached. In this state the intensity of radiation of frequency ν, i.e. K_ν, is equal to the intensity of the black radiation for the particular temperature. The mean value of the energy of the oscillator, i.e. $\bar{U}$, is found to be proportional to K_ν.

Using the laws of classical electrodynamics, Planck established the fundamental relation

$$K_\nu = \frac{\nu^2}{c^2}\bar{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 67$$

or from 14

$$u_\nu = \frac{8\pi\nu^2}{c^3}\bar{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 68$$

According to Wien's radiation law

$$K_\nu = a\frac{\nu^3}{c^2}e^{-\frac{\beta\nu}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 66$$

and the displacement law

$$K_\nu = \frac{\nu^3}{c^2}f\left(\frac{T}{\nu}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 49$$

Hence from these last two equations we should expect $\bar{U}$ to have the forms

$$\bar{U} = ave^{-\frac{\beta\nu}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 69$$

and

$$\bar{U} = \nu f\left(\frac{T}{\nu}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 70$$

Planck decided to attack the determination of $\bar{U}$ in his original relation above, through thermodynamics, and conceived the

[1] *Sitzungsber. K. Akad. Wiss. Berlin*, 1899, 455; 1895, 289–301; 1896, 151–170; 1897, 57–68; 1897, 715–717; 1897, 1122–1145; 1898, 449–476; 1901, 544–555; *Wied. Ann.* 1896, **57**, 1–14; 1897, **60**, 577–599. *Drude's Ann.* 1901, **6**, 818–831; 1900, **1**, 719–737.

[2] H. Hertz, *Wied. Ann.* 1889, **36**, 1.

idea of connecting the entropy [1] and not the temperature of the resonator with the energy. As at this stage he was not in a position to follow up the work by the connection of entropy and probability, use was made of Wien's Law together with Kirchhoff's Law and the second law of thermodynamics.

Planck obtained for the entropy S the expression

$$S = -\frac{\bar{U}}{\beta\nu}\left\{\log\left(\frac{\bar{U}}{a\nu}\right) - 1\right\} \quad . \quad . \quad . \quad . \quad . \quad 71$$

Applying the second law of thermodynamics in the form

$$dS = \frac{d\bar{U}}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 74$$

the result is obtained

$$\bar{U} = a\nu e^{-\frac{\beta\nu}{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 69$$

and this, combined with 67, again gives us Wien's Law.

From 71 above the remarkable relation is found that the reciprocal of the second differential coefficient of the entropy with respect to energy is proportional to the energy,

i.e.
$$\frac{d^2S}{d\bar{U}^2} = -\frac{b}{\bar{U}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 72$$

Calling this reciprocal R, we can write

$$R = 1\Big/\frac{d^2S}{d\bar{U}^2} = -b\bar{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad 73$$

Planck for a long time considered that this striking relation should be the foundation of a general law of radiation.[2]

We have seen however that the experimental work of Lummer and Pringsheim definitely proved that Wien's Law was valid only for short wave-lengths and high temperatures, while the work of Rubens and Kurlbaum [3] on long waves, infra-red waves, transmitted through fluorspar and sylvine, showed that $\bar{U} = cT$.

This with 74 gives

$$\frac{d^2S}{d\bar{U}^2} = -\frac{1}{T^2} = -\frac{c}{\bar{U}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad 75$$

hence
$$R = -\frac{\bar{U}^2}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 76$$

[1] Entropy in the second law of thermodynamics corresponds to energy in the first law, and may be defined as that thermal property of a substance which remains constant when the substance assumes different states without gaining or losing heat. If a body gains or loses an amount of heat dQ at temperature T, the change of entropy dS is denoted by dQ/T.

[2] *Drude's Ann.* 1900, **1**, 719.

[3] *Sitzungsber. K. Akad. Wiss. Berlin*, 1900, 929.

i.e. R is proportional not to the energy but to the square of the energy. Two limits have thus been set to R, which led Planck [1] to express R as the sum of two terms, one involving the first power, and the other the second power of the energy,

i.e. $$R = -b\bar{U} - \frac{\bar{U}^2}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 77$$

Integrating, we have

$$\frac{1}{T} = \frac{dS}{d\bar{U}} = \frac{1}{b}\log\left(1 + \frac{bc}{\bar{U}}\right) \quad . \quad . \quad . \quad . \quad 78$$

Hence $$\bar{U} = \frac{bc}{e^{\frac{b}{T}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 79$$

It will be noticed that this result has been arrived at by interpolation of purely empirical relations. Before describing the work leading to Planck's final formulæ and the conception of quanta, we shall deal with an important law due to Rayleigh, and developed by Jeans, which in its turn leads to a crucial test of the applicability of classical mechanics to radiation.

[1] For Planck's first result cf. *Verh. deutsch. physikal. Ges.* 1900, 202; cf. also *ibid.* 1900, 237; *Drude's Ann.* 1901, **4**, 553 and 564; 1901, **6**, 818; 1902, **9**, 629.

V

THE RAYLEIGH-JEANS LAW

Lord Rayleigh, in the year 1900, suggested a law[1] which is found to agree satisfactorily with experimental results in the case of long wave-lengths or low frequencies. Rayleigh's original argument may be summarized shortly as follows :— He points out that speculation is hampered by differences concerning the partition of energy deduction by which every mode of variation should be alike favoured, and for his line of reasoning considers a transversely vibrating string. According to Boltzmann and Maxwell the energy should be equally divided among all the modes, whose frequencies are as $1 : 2 : 3$. If k is the reciprocal of λ $\left[\lambda = \frac{1}{K}\right]$ then the energy limits between K and $K + dK$ is represented by dK.

For three dimensions, e.g. a cubical mass of air,

$$K^2 = p^2 + q^2 + r^2$$

where p, q and r are integers representing the number of subdivisions in three directions. We regard p, q, r as co-ordinates of points forming a cubic array, K being the distance of any point from the origin. Thus the number of points for which K lies between K and $K + dK$ is proportional to the volume of the corresponding spherical shell, and may be replaced by $K^2 dK$, and this expresses the distribution of energy according to the Boltzmann-Maxwell Law, as regards wave-length and frequency. Applying this to radiation, then since the energy of each mode is proportional to T, the energy distribution will be expressed by $Tk^2 dK$ or $T\frac{d\lambda}{\lambda^4}$. It is suggested that this is correct rather than Wien's expression, which can be written $C\lambda^{-5}e^{-\frac{c}{\lambda T}}d\lambda$ when λT is great. Rayleigh's complete expression can be written $CT\lambda^{-4}e^{-\frac{c}{\lambda T}}d\lambda$.

This law was subsequently developed on more rigid dynamical

[1] *Phil. Mag.* 1900 [v], **49**, 539.

lines by J. H. Jeans.[1] A useful expression for Rayleigh's Law should be noted:

From the quantitative expression of Maxwell's equipartition law the mean kinetic energy for f degrees of freedom is $f\frac{1}{2}k\mathrm{T}$. In the case of a point oscillator $f = 1$ and the total mean energy will consist of kinetic and potential energy in equal amounts, hence from 54 $\mathrm{U} = k\mathrm{T}$.

Combining this with Planck's relation

$$\mathrm{K}_\nu = \frac{\nu^2}{c^2}\mathrm{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 67$$

we have

$$\mathrm{K}_\nu = \frac{\nu^2}{c^2}k\mathrm{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 81$$

Up to now we have studied the application of Maxwell's distribution of energy law to the molecules of a radiating body and to a system of oscillators. Jeans and Rayleigh discuss the application of this law to the radiation itself and to the ether of space in the enclosure, and ultimately show that a law is obtained which cannot be reconciled to the results of experience and of experiment.

A Crucial Test of the Classical Laws.—In studying the exchange of energy of radiation between matter and ether we naturally have to consider an equilibrium state, in which the energy of the radiating system is in equilibrium with the energy of the enclosure, and for any temperature, calculate the most probable distribution of the energy between the various wave-lengths, which in the equilibrium state will be the actual distribution. Now if the ether is a structureless continuous medium it is capable of vibrating in an infinite number of modes, i.e. its number of degrees of freedom will be infinite, and it will sustain all possible wave-lengths between zero and infinity. Radiating matter, on the other hand, must, as we have seen, have a finite number of degrees of freedom. Hence on the equipartition principle the whole of the energy of the medium will be distributed among the infinite number of degrees of freedom of the ether, i.e. the system would lose the whole of its energy to the ether.

The following useful analogy is due to Jeans :— If a system of lightly connected corks is set in violent oscillation and allowed to float on the surface of water initially at rest, the motion of the corks will set up waves in the water, and these waves will spread over the surface, their energy ultimately being dissipated

[1] *Phil. Mag.* 1905 [vi], **10**, 91 ; 1909 [vi], **17**, 229 ; *Nature*, 1905, **72**, 94 and 243.

as heat energy to the water. Experience tells us that the corks will finally come to rest. It is impossible to imagine that they will continue to oscillate violently for an indefinite length of time. In the same way a system of small suspended masses oscillating in air must ultimately come to rest, having dissipated their energy to the surrounding medium of air.

Let us consider what these results would involve in the particular case of radiation. Consider a mass of metal at 0° C. in an impervious enclosure. For a mass of iron in the equilibrium state at this temperature, the heat energy of the iron is of the order 2×10^{14} times the energy density of the radiation in the enclosure; so that practically the whole of the heat energy resides in the atomic oscillations of the metal. For a structureless ether, instead of almost the whole energy residing in the comparatively few degrees of freedom of the iron, it should be distributed among the infinite number of degrees of freedom of the ether, hence the iron should lose all its energy until its temperature reached absolute zero, the temperature to be expected for the medium, and no equilibrium would be possible until the iron had lost the whole of its energy to the ether. This of course is entirely contrary to actual experience and experimental evidence.

Jeans considered the radiation itself in an enclosure and distributed its total energy according to the equipartition law over the individual degrees of freedom of the radiation or the possible vibrations in the enclosure. Lorentz [1] and later Jeans [2] made deductions in the case of free electrons moving through the interstices of matter and emitting radiation in encountering the atoms of the matter. The general result of applying classical dynamics to determine the conditions for the partition of radiant energy in a steady state of equilibrium with matter in the various cases of resonators, free electrons, and electrons encountering atoms [3] is to establish a general equation giving the density of radiant energy per unit volume as

$$\mathrm{E}(p)dp = \frac{\mathrm{RT}}{\pi^2 c^3} p^2 dp. \quad . \quad . \quad . \quad . \quad . \quad . \quad 82$$

where R is the gas constant, T is the absolute temperature of the matter, c is the velocity of light, and the frequency of the resonator or electron is $p/2\pi$. If the above relation is transformed to give the partition of radiant energy according to wave-

[1] "On the Emission and Absorption by Metals of Rays of Heat of great Wave-length," *K. Akad. Wetensch.*, Amsterdam, 1903, **5**, 662.

[2] *Phil. Mag.* 1909, 773; 1909, 209; 1909 [vi], **17**, 773; **18**, 209.

[3] *Phil. Mag.* 1909 [vi], **18**, 209; 1907 [vi], **14**, 225.

length, and the energy in a small range $d\lambda$ is denoted by $f(\lambda T)d\lambda$, then since $\lambda = 2\pi c/p$ we have

$$f(\lambda T)d\lambda = 8\pi RT\lambda^{-4}d\lambda. \quad . \quad . \quad . \quad . \quad . \quad 83$$

This corresponds to Jeans' result for the free vibrations in an enclosure, as it is shown that the general equation for the number of free vibrations per unit volume of a medium is

$$C\lambda^{-4}d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 84$$

The value of the constant c [1] for sound vibrations in a gas is 4π, for the vibrations of light in free ether 8π, and for vibrations in an elastic solid 12π; the ratio of these three values is therefore 1 : 2 : 3; the explanation of this being that a sound wave is determined by one vector, i.e. displacement in the direction of propagation, there being only one set of normal vibrations; a light wave is determined by two vectors, there being two independent transverse vibrations in different planes of polarization for each normal vibration in the gas, while in an elastic solid both normal and transverse vibrations are possible, hence the value required is the sum of the previous two.

From our radiation formula 83 if the number of vibrations is $8\pi\lambda^{-4}d\lambda$ the average energy of each vibration is RT.

Analysis of the Rayleigh-Jeans Law.—A graphical representation of the Rayleigh-Jeans formula 83 gives a curve which contains no maximum, but rises rapidly as λ diminishes. Integrating between $\lambda = 0$ and $\lambda = \infty$ we should obtain an expression for the total radiant energy of the enclosure. This integral is infinite, so that the ether should contain an infinite amount of energy for any finite value of T. For a finite value of the energy we should require $T = 0$. In short, for finite values of T, the whole of the energy of the matter would tend to pass into energy of space.

As to the nature of the ether, if it exists, there are the alternatives that it is structureless or else possesses so fine a structure as to have escaped observation. If wave motion is to be propagated in a medium, the waves cannot be shorter than the distance apart of the particles composing the medium, otherwise no propagation would be possible. Hence the shortest light waves must be large compared to the structure of the ether itself. Referring to the form of the Rayleigh-Jeans expression in the case of a system of molecules, the energy distribution being given by $4\pi RT\lambda^{-4}d\lambda$: if in deference to the above considerations we consider a range of wave-lengths from λ_0 down

[1] H. A. Lorentz, *The Theory of Electrons*, § 73; *Phil. Mag.* 1905 [vi], **10**, 91; H. Weyl, *Math. Annalen*, **71**, 441.

to a limiting wave-length λ_m and integrate between these limits, we have for the total energy

$$\frac{4\pi RT}{3\lambda^3_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 85$$

From this we see that only one-eighth of the total energy will be of wave-length greater than $2\lambda_m$, and seven-eighths will be of wave-length between $2\lambda_m$ and λ_m. For an enclosure containing air λ_m will be of the order 10^{-7} and only one-millionth part of the total energy will be of wave-length greater than 10^{-5}; actually the greater part lies in the region 10^{-4}.

In short, classical dynamics shows that the energy passes into the smallest wave-lengths which the medium is capable of sustaining. Actual experiment, as we have seen, indicates that distribution does exist and that the maximum energy is certainly not located in the shortest wave-lengths, but that only a very small part of the energy is distributed among the very short or very long waves, the maximum being among those of intermediate length. For radiation in equilibrium with a black body at ordinary temperature the maximum lies in the infra-red region, and is vanishing by small or either extremes of wave-length. All this is clearly shown by the curves in Fig. 2 exhibiting a definite maximum. Hence whether the number of degrees of freedom of the ether is infinite or not, we are led to conclude that the equipartition principle is not applicable to the partition of radiant energy between ether and matter.

Against all that has been said, certain objections might be urged which are worth short consideration.[1] The system of corks previously suggested for analogy were oscillating in a material medium, whereas it might be insisted that the radiating system is in a non-material ether, so that possibly the principles of classical mechanics are not at fault, but that our argument goes to prove the ether non-existent. As Jeans has pointed out, this fundamental problem cannot be solved on such simple considerations. Relativity principles do not disprove the existence of an ether but simply show that results are the same whether the ether exists or not. Or again, can energy ever be in equilibrium with matter at all, or can energy be dissociated from matter? It is also suggested that true equilibrium is never reached because no enclosure is absolutely impervious to energy of the highest frequencies, which therefore always escapes. Against accepting this view is the fact that final results are so completely independent of the nature of the walls of the enclosure.

[1] Cf. also *Phil. Mag.* 1910 [vi], **20,** 642; 1908 [vi], **16,** 353.

VI

PLANCK'S LAW OF RADIATION

The position which has been arrived at is that two laws of radiation have been formulated: one of them, Wien's law, being satisfactory for high frequencies or short wave-lengths; the other, the Rayleigh-Jeans law, being satisfied by low frequencies or long wave-lengths, but neither laws of universal application of all wave-lengths. The idea naturally arises of supposing that these two laws must be special cases of a perfectly general law of radiation. It has been mentioned that Planck, at the time of his earlier calculations which have been discussed, was not in a position to attack the problem further on the lines of the connection between entropy and probability; he however followed up the idea of a connection between these two quantities. Entropy is a measure of physical probability as regards the second law of thermodynamics, for the more often a condition occurs the more probable it is. He ultimately availed himself of an extremely useful connection between entropy and probability of a state, due to Boltzmann,[1] and which may be written

$$S = k \log W. \quad . \quad . \quad . \quad . \quad . \quad . \quad 86$$

In deducing this shortly we may say that for any spontaneous process both the entropy of the system concerned and the thermodynamic probability of its state tend to reach a maximum value. Assuming a connection between the two we can write

$$S = f(w)$$

where S is the entropy of any state for which w is the corresponding thermodynamic probability. To evaluate the function let us consider two independent systems in different states for which the entropy and corresponding probability are s_1 and s_2, w_1 and w_2 respectively, then

$$s_1 = f(w_1) \qquad\qquad s_2 = f(w_2)$$

The total entropy of the two systems will be

$$S = s_1 + s_2 = f(w_1) + f(w_2)$$

[1] Cf. Boltzmann's H-Theorem, *Vorlesungen über Gastheorie*, I. 1896, 38; *Sitzungsber. K. Akad. Wiss. Wien*, 1877, **76**, 373. Cf. Jeans' *Dynamical Theory of Gases*.

Now the actual state we are considering for the first system can be realized by selecting any one of the w_1 complexions of that particular state, and similarly for any of the w_2 complexions of the second system. Then for the combined system the state can be realized by selecting any one of the w_1 complexions of the first and any one of the w_2 complexions of the second and combining these two. Thus for the combined system the probability is given by $w_1 \times w_2$, hence

$$S = f(w_1 w_2).$$

Also we have seen $S = f(w_1) + f(w_2)$.

To satisfy these two equations the function must obviously be a logarithmic one,

i.e. $$\log w_1 w_2 = \log w_1 + \log w_2.$$

Thus $$S \propto \log W$$

or $$S = k \log W. \quad . \quad . \quad . \quad . \quad . \quad 86$$

Writing it in its most general form

$$S = k \log W + \text{a constant} \quad . \quad . \quad . \quad . \quad 87$$

It can easily be shown thermodynamically that the value of the constant k is

$$k = \frac{R}{N}$$

i.e. k is the gas constant per molecule. (Cf. 54.)

A fundamental step is that whereas Boltzman leaves the additive constant undetermined, Planck assigns a definite absolute value to S. He points out that just as differences of energy and not absolute energy are measured, so we are always concerned with differences of entropy and not absolute entropy; we can however define an absolute value for S and hence for probability if the additive constant is so fixed that entropy and energy vanish simultaneously; as W is greater than unity, S will be a positive term becoming zero at absolute zero. This is considered later in connection with the Nernst Heat Theorem.

The Hypothesis of Quanta.—Planck decided to modify the expression for the mean energy of an oscillator.[1] Whereas the distribution of energy among the oscillators has always been regarded as taking place perfectly continuously, Planck divides the energy of the enclosure into a number of discrete, finite

[1] The important paper marking the foundation of the Quantum Theory: *Drude's Ann.* 1901, **4**, 553.

elements of energy, or energy bundles (quanta) each of magnitude ε. To the distribution of these quanta he applies the ordinary laws of probability. Each distribution corresponds to a definite state of the system, hence each condition may be realized in a number of different ways, this number being the thermodynamic probability of the condition considered. Boltzmann's probability-entropy relation is then employed to connect the probability obtained with the entropy of the system of oscillators. The second law of thermodynamics finally enables a connection to be made between the quantities $\bar{U}$, ε and the absolute temperature T.

Let N oscillators be present, possessing a total energy U_N. If $\bar{U}$ is the mean energy of an oscillator, then

$$U_N = N\bar{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 88$$

We divide the energy U_N into P energy elements ε so that

$$U_N = N\bar{U} = P\varepsilon \qquad \text{i.e.} \qquad P = N\frac{\bar{U}}{\varepsilon}$$

Now the number of ways of distributing P elements among N oscillators is

$$\frac{\lfloor N + P - 1}{\lfloor N - 1 \quad \lfloor P}$$

This number of such distributions (W) is called the thermodynamic probability of the condition in question. By Boltzmann's relation

$$S_N = k \log W. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 86$$

i.e.
$$S_N = k \log \left\{ \frac{\lfloor N + N\frac{\bar{U}}{\varepsilon} - 1}{\lfloor N - 1 \quad \lfloor N\frac{\bar{U}}{\varepsilon}} \right\} \quad . \quad . \quad . \quad . \quad 89$$

Since N and P are very large, we may apply Stirling's formula,[1] hence

$$S_N = kN\left\{\left(1 + \frac{\bar{U}}{\varepsilon}\right) \log \left(1 + \frac{\bar{U}}{\varepsilon}\right) - \frac{\bar{U}}{\varepsilon} \log \frac{\bar{U}}{\varepsilon}\right\} \quad . \quad . \quad 90$$

Therefore the entropy S of *one* oscillator becomes

$$S = \frac{S_N}{N} = k\left\{\left(1 + \frac{\bar{U}}{\varepsilon}\right) \log \left(1 + \frac{\bar{U}}{\varepsilon}\right) - \frac{\bar{U}}{\varepsilon} \log \frac{\bar{U}}{\varepsilon}\right\} \quad . \quad 91$$

[1] According to Stirling's formula, if N is large $\log \lfloor N = N \log N - N$.

But by the second law of thermodynamics $dS/dU = 1/T$,

hence $$\frac{1}{T} = \frac{dS}{dU} = k\left\{1 + \frac{1}{\varepsilon}\log\left(1 + \frac{\bar{U}}{\varepsilon}\right) - 1 - \frac{1}{\varepsilon}\log\frac{\bar{U}}{\varepsilon}\right\}$$

$$= \frac{k}{\varepsilon}\log\frac{1 + \frac{\bar{U}}{\varepsilon}}{\frac{\bar{U}}{\varepsilon}} = \frac{k}{\varepsilon}\log\left(1 + \frac{\varepsilon}{\bar{U}}\right) \quad . \quad . \quad . \quad . \quad 92$$

i.e. $$\log\left(1 + \frac{\varepsilon}{\bar{U}}\right) = \frac{\varepsilon}{kT} \quad . \quad . \quad . \quad . \quad . \quad 93$$

i.e. $$1 + \frac{\varepsilon}{\bar{U}} = e^{\frac{\varepsilon}{kT}}$$

i.e. $$\bar{U} = \frac{\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} \quad . \quad . \quad . \quad . \quad 94$$

Now from Wien's displacement law

$$\bar{U} = \nu f\left(\frac{\nu}{T}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad 70$$

That these last two relations should be satisfied the essential condition is that ε must be made proportional to ν;

i.e. $$\varepsilon \propto \nu$$

or $$\varepsilon = h\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 95$$

This then is the fundamental equation of Planck's Quantum Theory. Its larger significance will be later discussed. Substituting now in the expression for $\bar{U}$ we have

$$\bar{U} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 96$$

From the laws of classical electromagnetics Planck, as we have seen, had obtained

$$K_\nu = \frac{\nu^2}{c^2}\bar{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 67$$

or $$u_\nu = \frac{8\pi}{c}K_\nu = \frac{8\pi\nu^2}{c^3}\bar{U} \quad . \quad . \quad . \quad . \quad 68$$

It should be particularly noted that the disputed point has been the value of $\bar{U}$. Hence we may write

$$K_\nu = \frac{h\nu^3}{c^2} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 97$$

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu \quad . \quad . \quad . \quad . \quad 98$$

and $$E_\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{\lambda KT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 99$$

which are forms of Planck's well-known law of radiation.

The fundamental feature of the Quantum Theory is that it rejects the principle of equipartition of energy, which assumes a perfectly continuous exchange of energy. Planck assumes that exchange of energy between matter and ether can take place only discontinuously or in discrete units or integral multiples of a small energy unit. It should be noted that he does not assert that the energy itself has a discontinuous or discrete unitary structure ; rather he confines his considerations to the mode of absorption and emission of energy by matter. A Planck resonator will not react with an infinitely small amount of energy ; the energy must attain a finite value ε before the resonator of the material system can absorb or emit it. Now any particular degree of freedom cannot be associated with less than one quantum ε of energy, and will actually be associated with an integral multiple of ε. Hence some of the degrees of freedom may possess no energy at all. This helps to explain the failure of the equipartition theory.

The energy ε is not a fixed quantity but is directly proportional to the vibration frequency of the radiation, or to the frequency of the resonator, this being clear from the fundamental relation $\varepsilon = h\nu$. The universal constant is h (Planck's constant), and has the dimensions [energy $\times$ time], i.e. action, thus often referred to as the quantum of action :

$$h = 6{\cdot}55 \times 10^{-27} \text{ erg-seconds.}$$

In a spectrum of radiation due to a system of electromagnetic oscillators, for the very short wave-lengths or high frequencies the value of ε must be large ; the probability of an oscillator possessing so large a quantum is less than in the case of a smaller quantum corresponding to intermediate wave-lengths ; hence the energy due to very short waves will be small. Again for very long waves and low frequencies, ε will be small, thus the energy from very long waves will be small. A resonator can therefore avail itself only of large energy units at high frequencies and small energy units at low frequencies, so that the radiation will contain comparatively little energy corresponding to very short or very long waves, but mainly energy of intermediate waves. This is precisely what is found experimentally, as we have seen from the curves in Fig. 2.

Planck's Law has been confirmed satisfactorily by Rubens and

Kurlbaum [1] for long waves, and by Paschen for short waves.[2] Much work on black radiation has also demonstrated the validity of the law.[3]

The law contains Wien's relation $E_{\lambda\,max} = \text{constant} \times T^5$, for from p. 26.

$$E_{\lambda max} = C\lambda^{-5} = CT^5.$$

Again, differentiating the original expression with respect to λ and equating to zero for λ_{max}, we have

$$\frac{hc}{\lambda kT} = 4{\cdot}9651$$

i.e. $\lambda_{max}T = \dfrac{hc}{k.4{\cdot}9651} = \text{Wien's constant } (\cdot 294 \text{ cm. degree}).$

Hence $\dfrac{h}{k} = \dfrac{4{\cdot}9651 \times {\cdot}294}{3 \times 10^{10}} = 4{\cdot}866 \times 10^{-11}.$

For the total radiation we have

$$K = 2\int K_\nu d_\nu = \frac{2h}{c^2}\int \frac{\nu^3 d\nu}{e^{\frac{\nu h}{kT}} - 1} = \frac{2\pi^4 k^4}{15c^2h^3}T^4 = \text{constant } T^4$$

or Stefan's total radiation law.

Stefan's Law gives us $K = \sigma T^4$, where K is the total energy radiated per second from 1 sq. cm. of a black body. In one second the radiation travels 3×10^{10} cm., hence the volume of the radiation is 3×10^{10} cc. The space density of the energy is therefore

$$\frac{K}{3 \times 10^{10}} = E, \text{ or } K = 3 \times 10^{10}E.$$

For a black body at 1° absolute and surroundings at 0° absolute, we have

$$3 \times 10^{10}E = \sigma$$

i.e. $E = \dfrac{\sigma}{3 \times 10^{10}} = \dfrac{22{\cdot}89 \times 10^{-5}}{3 \times 10^{10}} = 7{\cdot}061 \times 10^{-15}$ erg/cc.

Since $T = 1$ we can write

$$E = \int E_\lambda d\lambda = \int u_\nu d\nu = \frac{8\pi h}{c^3}\int \frac{\nu^3 d\nu}{e^{\frac{h\nu}{k}} - 1} = \frac{8\pi}{c} \cdot \frac{\pi^4 k^4}{15c^2h^3}$$

[1] Rubens and Kurlbaum, *Sitzungsber. K. Akad. Wiss. Berlin*, 1900, 929; *Drude's Ann.* 1901, **4**, 649.

[2] Paschen, *ibid.* 277.

[3] Coblentz, *Phys. Rev.* 1910 [i], **31**, 317; Warburg and collaborators, *Ann. Physik.* 1913 [iv], **40**, 609; 1915 [iv] **48**, 410.

Putting this equal to E above,

$$\frac{k^4}{h^3} = \frac{15c^3}{8\tau^5} \cdot 7{\cdot}061 \times 10^{-15} = 1{\cdot}1684 \times 10^{15}$$

and combining this with

$$\frac{h}{k} = 4{\cdot}866 \times 10^{-11}$$

we obtain $h = 6{\cdot}55 \times 10^{-27}$ erg/sec.

$k = 1{\cdot}346 \times 10^{-16}$ erg/degree.

Comparison of Planck's Result and Newtonian Mechanics.—On comparing the radiation law based on classical grounds with Planck's Law, the essential differences of which lie in the expression for the mean energy of an oscillator, we see that classical statistics give us

$$\bar{\mathrm{U}} = k\mathrm{T}$$

whereas the Quantum Theory gives us

$$\bar{\mathrm{U}} = \frac{h\nu}{e^{\frac{h\nu}{k\mathrm{T}}} - 1}$$

The difference between these two is therefore the factor [1]

$$\frac{\frac{h\nu}{k\mathrm{T}}}{e^{\frac{h\nu}{k\mathrm{T}}} - 1}$$

or writing $\frac{h\nu}{k\mathrm{T}} = x$ we have

$$\frac{x}{e^x - 1}$$

The expansion of this gives us

$$\frac{x}{x + \frac{x^2}{\lfloor 2} + \frac{x^3}{\lfloor 3} + \frac{x^4}{\lfloor 4} + \ldots}$$

or

$$\frac{1}{1 + \frac{1}{2}x + \frac{1}{6}x^2 + \frac{1}{24}x^3 + \ldots}$$

From this expansion it is clear that the energy given by Planck's formula is always less than that of the classical formula, the divergence between the two increasing as x increases.

[1] Some interesting discussions on this factor have been given: Cf. *Nature*, 1925, **115**, 798, 838.

To show that Planck's Law contains Wien's and Rayleigh's Laws as special cases:

For short wave-lengths or high frequencies and high temperatures, or more exactly for high values of $\frac{h\nu}{k\mathrm{T}}$, the limit of $1/e^{\frac{h\nu}{k\mathrm{T}}}-1$ becomes $1/e^{\frac{h\nu}{k\mathrm{T}}}$ or $e^{-\frac{h\nu}{k\mathrm{T}}}$ and so passes over into the form of Wien's Law. On the other hand, for long wave-lengths and low frequencies, or small values of $\frac{h\nu}{k\mathrm{T}}$,

$$\frac{h\nu}{e^{\frac{h\nu}{k\mathrm{T}}}-1} = \frac{h\nu}{1+\frac{1}{2}\frac{h\nu}{k\mathrm{T}}}$$

which, if ν is small, becomes $k\mathrm{T}$, giving us Rayleigh's Law.

Calculating Avogadros number N from $k = \mathrm{R}/\mathrm{N}$, using the value of k found from radiation data, it is found that

$$\mathrm{N} = 6{\cdot}175 \times 10^{23}$$

which is in remarkably good agreement with the most accurate results of Millikan, obtained by entirely different methods. This leads to e, the electron charge, the value of which, calculated by Planck, from his theory differs very slightly from Millikan's value. These remarkable results give very strong support for the quantum theory of radiation.

Planck subsequently found it necessary to modify his original views, for according to his second theory, while emission can take place only discontinuously, absorption can take place continuously. It is only to be expected that a general theory so revolutionary as that of Planck would meet with various difficulties. This will be seen, for instance, in its extension to the theory of light, which is difficult to reconcile with the classical undulatory theory.

In the second part of this book will be found a full discussion of Planck's later views, the extension of the theory to light, and its development by Einstein, together with its application to a number of physical problems.

PART II

THE DEVELOPMENT OF THE QUANTUM THEORY

VII

THE LIGHT-QUANTUM HYPOTHESIS

Light-Quantum Hypothesis. It is fairly certain that if the Quantum Theory had been found to be confined to its original sphere in the realm of radiation, it would never have reached the position of importance and prominence in theoretical physics which it holds to-day. This prominence is largely due to the remarkable way in which the theory has helped to elucidate problems with which it is at first sight apparently entirely unconnected. It has been truly said that the theory is less an attempt to explain, than a focussing of all difficulties into one, so that if this master-difficulty is overcome, a number of others melt away.[1] While admiring its wonderful utility we shall however be forced to admit that the main disappointment of the theory lies in its inability to bring us to an actual understanding of the ultimate underlying cause of the discontinuity which it postulates, or to an explanation of the mechanisms with which it deals. The difficulty of formulating a satisfactory physical basis is the only serious objection which can be urged against the theory ; but we shall finally return to this point after considering a variety of evidence and applications.

The first outstanding application of the theory was due to Einstein [2] in his light-quantum hypothesis. Planck, as we have remarked, preferred to confine the function of quanta to the interaction of radiation and matter, without reference to the structure of radiation itself.

[1] W. H. Bragg.

[2] *Drude's Ann.* 1905, **17**, 132; *Ann. Physik*, 1906 [iv], **20**, 199.

Einstein, on the other hand, was led to postulate that radiation, when propagated through a vacuum or any medium, possesses a quantum-like structure, so that energy, instead of being propagated as waves, exists as finite energy complexes which can be emitted and absorbed only as individuals. This theory is not without serious difficulties, and has not met with universal acceptance.

Basis of Einstein's Light-Quantum Hypothesis.—The first basis of the hypothesis is an analogy of spatial distribution of radiation to the spatial distribution of gas molecules. If a volume V of gas contains n molecules, the probability that all these shall be at a given moment confined to a fractional volume v of the whole is

$$w = \left(\frac{v}{\mathrm{V}}\right)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad 100$$

If E is the total energy of monochromatic radiation of frequency ν, where ν is so large and the temperature T so low that Wien's Law is valid, then the probability of a similar spatial distribution is

$$w = \left(\frac{v}{\mathrm{V}}\right)^{\frac{\mathrm{E}}{h\nu}} \quad . \quad . \quad . \quad . \quad . \quad . \quad 101$$

Hence $n = \mathrm{E}/h\nu$, i.e. the energy consists of n complexes, each of magnitude $h\nu$. Secondly,[1] if E is the momentary energy of black-body radiation of frequency ν in a small volume v communicating with a large volume, the fluctuation of the energy about a mean value $\bar{\mathrm{E}}$ is given by $\varepsilon = \mathrm{E} - \bar{\mathrm{E}}$.

From general statistics we have

$$\bar{\varepsilon}^2 = k\mathrm{T}^2\frac{d\bar{\mathrm{E}}}{d\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad 102$$

where $\bar{\varepsilon}^2$ is the mean square of the impulse fluctuations.

If we substitute $\bar{\mathrm{E}} = vu_\nu d\nu$, then

$$\bar{\varepsilon}^2 = k\mathrm{T}^2 v d\nu \frac{du_\nu}{d\mathrm{T}} = \frac{8\pi h^2\nu^4 v d\nu e^{\frac{h\nu}{k\mathrm{T}}}}{c^3(e^{\frac{h\nu}{k\mathrm{T}}} - 1)} \quad . \quad . \quad 103 \text{ from } 98$$

From 98 we also have

$$e^{\frac{h\nu}{k\mathrm{T}}} = 1 + \frac{8\pi h\nu^3}{c^3 u_\nu} \quad . \quad . \quad . \quad . \quad . \quad 104$$

Then, substituting,

$$\bar{\varepsilon}^2 = u_\nu v d\nu h\nu + \frac{c^3 u_\nu^2 v d\nu}{8\pi\nu^2} \quad . \quad . \quad . \quad . \quad . \quad 105$$

$$= \bar{\mathrm{E}}h\nu + \frac{c^3(\bar{\mathrm{E}})^2}{8\pi\nu^2 v d\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad 106$$

[1] *Phys. Zeitschr.* 1909, **10**, 185.

Of the two terms in this expression the second predominates under the conditions of validity of Wien's Law, and for each point in the volume v, the intensity and hence the energy varies continuously. To explain the first term, however, the energy must be supposed to consist of a number of energy complexes, each of value $h\nu$, for which $\bar{\mathrm{E}} = \bar{n}.h\nu$ where $\bar{n}$ is the mean about which n varies.

From the variation $n - \bar{n}$ we have $\varepsilon = \mathrm{E} - \bar{\mathrm{E}} = (n - \bar{n})h\nu$ and $\bar{\varepsilon}^2 = (n - \bar{n})^2 h^2\nu^2$. But statistically $(n - \bar{n})^2 = \bar{n}$, hence $\bar{\varepsilon}^2 = \bar{n}h^2\nu^2 = \bar{\mathrm{E}}h\nu$. The first term therefore requires for its explanation the conception of energy quanta. Thirdly, if a freely movable reflecting plate is in equilibrium under, on the one side, the impulses of a field of black radiation, due to irregular fluctuations of radiation pressure, and on the other side the irregular impulse of gas molecules, there follows for $\bar{\varepsilon}^2$ an expression of two terms which requires for its explanation considerations similar to the above.

Such are, shortly, results on which Einstein's light quantum hypothesis is based.

The theory furnishes a striking explanation of the phenomena of phosphorescence, fluorescence, excitation of Röntgen rays and the photo-electric effect.

In the case of phosphorescence or the transformation of light into that of another frequency, if light of frequency ν_e causes the emission of phosphorescent light of frequency ν_p, Einstein states that one quantum $h\nu_e$ of exciting radiation is changed through absorption by the atom of the phosphorescent substance into one quantum $h\nu_p$ of phosphorescent light. This is in agreement with Stokes' Law $\nu_e > \nu_p$, leading from the above to $h\nu_e > h\nu_p$, i.e. the light is always transformed into light of lower frequency. Further support to Einstein's view is afforded by the fact that the emission of phosphorescent light is not instantaneous, for when the exciting light falls on the body the phosphorescence gradually rises to a maximum as the number of molecules excited increases. The molecules therefore do not all emit simultaneously but only as they are excited by the light energy complexes. This is contrary to the result which would be expected from the continuous wave front of the classical undulatory theory.

It is of interest to note that the views of Sir J. J. Thomson [1] on the structure of the light wave front give an explanation of the above phenomena, and also of the observed facts of the photo-electric effect discussed below. According to Thomson's

[1] *Proc. Camb. Phil. Soc.* 1908, **14**, 421.

view light travels in transverse vibrations along tensional lines of electric force in the ether (Faraday tubes), and the light energy is therefore concentrated in pulses along the wave front, a view in some degree analogous to the old emission theory.

Fluorescence.[1]—Whereas phosphorescence persists for a time after the removal of the exciting light, fluorescence ceases simultaneously. When the exciting agency is either Röntgen or visible rays, the fluorescent body shows a maximum absorption for a certain value of ν_e, and emits a spectrum, all the lines of which have a lower frequency than ν_e, so that again Stokes' Law holds, for the quantum of all emitted rays must be lower than the quantum of the exciting rays.

Photo-Electric Effect.—The photo-electric effect, or production of energy of motion by light, consists in the removal of electrons from bodies by the incidence of ultra-violet or rays of higher frequency such as Röntgen rays, although certain metals, e.g. the alkali metals, exhibit the effect under the influence of visible light. The photo-electric effect comprises the so-called normal and selective effects. The normal effect is independent of the orientation of the electrical vector of the light wave, while the selective effect depends on the plane of polarization of the incident light, and appears when the electrical vector of the light wave has, in the case of incidence on a metal surface, a component vertical to the surface, and shows a maximum at a definite wave-length.

The velocities of the ejected electrons may vary up to a maximum v depending only on the nature of the metal and the frequency of the incident light, but independent of the *intensity* of the light,[2] and apparently independent of the temperature,[3] as far as has been ascertained for the range over which experiments have been conducted. The magnitude of the effect, however, increases with the light intensity since the number of ejected electrons increases. For a given metal the maximum velocity of ejection increases with the frequency of the incident light, for frequencies above a critical value, the so-called threshold frequency, below which no ejection takes place.

If the energy of the incident radiation exists as quanta, and E is the energy required to eject an electron, then ejection can

[1] Barkla, *Phil. Mag.* 1904 [vi], **7**, 543; 1908 [vi], **15**, 288; 1908 [vi], **16**, 550; Barkla and Sadler, *Phil. Mag.* 1909 [vi], **17**, 739; de Broglie, *Compt. Rend.* 1914, **158**, 1785; Wagner, *Ann. Physik*, 1915 [iv], **46**, 868.

[2] Lenard, *Drude's Ann.* 1902, **8**, 149; Pohl and Pringsheim, *Ber. deutsch. physikal. Ges.* 1912, **15**, 974; Millikan, *Phys. Rev.* 1913 [ii], **1**, 73.

[3] Ladenburg, *Verh. deutsch. physikal. Ges.* 1907, **9**, 165; Lienhop, *Ann. Physik*, 1906 [iv], **21**, 281.

be effected only when $h\nu > E$; hence the critical frequency ν_0 is given by $h\nu_0 = E$.

For frequencies ν higher than ν_0, since the atom cannot absorb a fraction of the quantum and leave an unabsorbed fraction, it is assumed that the excess energy $h\nu - h\nu_0$ goes to supply kinetic energy to the ejected electron. This leads to an important relation—Einstein's law of photo electric effect

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad 107$$

where v is the maximum velocity and m the mass of the ejected electron. The function of $h\nu_0$ may be more fully described as the energy required to tear the electron from the atom and raise it from the point at which it was torn to the point at which it leaves the surface of the body.

If V is the ionization potential of the substance in question, i.e. the smallest voltage required to ionize it, or eject an electron, or give the electron the kinetic energy $\frac{1}{2}mv^2$, then $h\nu_0 = eV$, e being the electronic charge. A satisfactory verification of Einstein's law has been made, for the normal photo-electric effect of sodium and lithium by Millikan,[1] who calculated the value of h and found that the result accorded closely with the value obtained by Planck from radiation data. It should be noticed that Einstein's light-quantum hypothesis is not essential to the explanation of the photo-electric effect, for the same result follows from Planck's concept of quantum absorption and emission. The ionization of gases by ultra-violet light is also an example of photo-electric phenomena, where if J is the work required to ionize one gaseous molecule or to remove an electron from it, then $h\nu \geq J$.

In general, then, photo-electric phenomena may be described as the change of light-quanta into the kinetic energy of electrons ejected from a body, and may be explained on the basis of Einstein's Law.

In addition to the ultra-violet light photo-electric effect, there is also the X-ray photo-electric phenomenon, in which electrons are ejected from matter over which X-rays are allowed to pass. In contrast to the case of ultra-violet light for which the frequency ν is comparable to the threshold frequency ν_0, the value of ν for X radiations is some thousands of times greater than in the former case, and ν_0 becomes negligible.

Einstein's equation can now be applied in the form

$$\tfrac{1}{2}mv^2 = h\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 108$$

showing that the energy of the ejected electron is equal to the energy quantum of the incident X radiation.

[1] *Phys. Rev.* 1916 [ii], **7**, 362; *Phys. Zeitschr.* 1916, **17**, 217.

Electrons may also be ejected from matter by β-rays or electrons emitted from radioactive bodies, and further by α-rays or positively charged particles from radioactive substances. In such inelastic collisions occurring between the ionizing particle and the electron, as opposed to the elastic collisions of the kinetic theory, which involve no chemical change, the impact may cause the complete ejection of an electron, or the ionization of the atom bombarded. The ultimate return of the electron gives rise to an emission spectrum. The collision by the bombarding particle may however take place in such a way that the electron is not ejected but merely displaced from its normal orbit. Its return gives rise to the emission of a single frequency radiation and the potential which must be applied to the bombarding electron under such circumstances is termed the resonance potential in distinction to the ionization potential.

If we consider the lowest kinetic energy of the electron which will produce the effect, then practically the whole of its energy will be transferred at the impact and we have the relation

$$\tfrac{1}{2}mv^2 = h\nu_r$$

where ν_r is the frequency of the single line emitted, and if V_r is the resonance potential of the gas, then

$$\tfrac{1}{2}mv^2 = eV_r = h\nu_r \quad . \quad . \quad . \quad . \quad . \quad 109$$

which summarizes the quantum condition necessary for the phenomenon. This has been tested in the course of much recent work on ionization and resonance potentials.[1] An exactly similar relation is found to apply for ionization potentials :

$$\tfrac{1}{2}mv^2 = eV_i = h\nu_i \quad . \quad . \quad . \quad . \quad . \quad 110$$

where V_i is the ionization potential, and ν_i the greatest frequency of the radiation emitted.

Photochemical Reactions.[2]—The quantum theory has found an application to photochemical processes, which consist of chemical reactions due to the influence of high-temperature

[1] For the alkali metals : Tate and Foote, *Phil. Mag.* 1918 [vi], **36,** 64 ; Foote, Rognley and Mohler, *Phys. Rev.* 1919 [ii], **13,** 68.

For other metals : Mohler, Foote and Meggers, *Bull. Bur. Stand.* 1920, **16,** 725.

For helium : Franck and Knipping, *Phys. Zeitsch.* 1919, **20,** 481 ; Horton and Davies, *Proc. Roy. Soc.* 1919, **95A,** 408 ; *Phil. Mag.* 1920 [vi], **40,** 440.

Neon and argon : Horton and Davies, *Proc. Roy. Soc.* 1920, 98A, 124.

Hydrogen : Franck, Knipping and Krüger, *Ber. deutsch. physikal. Ges.* 1919, **21,** 728 ; Horton and Davies, *Proc. Roy. Soc.* 1920, **97A,** 23 ; Mohler and Foote, *Bull. Bur. Stand.* 1920, **16,** 669.

[2] An able survey of photochemistry from 1914–1925 is contained in *Annual Repts. Chem. Soc.* 1925, 333–373.

external radiation. After many attempts by various authors to deal with the theoretical side of the process thermodynamically, Einstein,[1] in 1912, formulated his law of the photochemical equivalent, which states that for the photochemical decomposition of each molecule of a substance by the absorption of radiation of frequency ν, there is required one quantum of energy $h\nu$. Einstein deduced this law, for the range of validity of Wien's law of radiation independently of the light-quantum hypothesis and on thermodynamic lines. Experimental evidence bearing on the law is conflicting, since on calculating the quantum efficiency or number of absorbing molecules which have reacted per quantum absorbed, in certain cases the theoretical value, unity, is obtained, in many cases the results are found to vary over a wide range, indicating that the amount of change is either much greater or much less than would be expected. The reason for this appears to be that the true effect is masked by other processes taking place simultaneously, also there is the probability of some of the radiation, degraded into longer wave radiation, introducing thermal complications. A further difficulty is the need for employment of a single definite frequency of radiation as required by the law, and which corresponds with the head of the absorption band of the substance.

Among the chief photochemical problems which have been investigated may be mentioned influence of concentration and pressure, intensity of light, velocity and temperature coefficients of reaction, and effects of traces of moisture. The photochemical reactions of chlorine in particular are of considerable interest and complexity, and in consequence have received a large share of attention. A review of the present position of photochemistry shows that a large mass of experimental and theoretical results have accumulated, which have not so far been correlated and which are in some cases conflicting. It has not been found possible to conform these results to a law having general application. This is partly due to an imperfect understanding of the mechanism of the reactions, and partly to the numerous subsidiary factors having an imperfectly defined bearing on any particular reaction.

As a specific instance may be mentioned the fact that owing to the different effects due to different parts of the spectrum it has been suggested on the one hand that two types of absorption band, photochemical and thermal, may exist, and on the other hand that a photosensitive substance may consist of one con-

[1] *Ann. Physik*, 1912 [iv], **37**, 832. See also *Ber. deutsch. physikal. Ges.* 1916, **18**, 318.

stituent absorbing purely thermally, and the other photosensitive. This problem is complicated by energy degradation due to possible intra- and inter-molecular perturbations. Attempts have been made, from quantum considerations, to calculate the threshold or critical frequency of photochemical reactions, but the results are inconclusive. In general a proportionality has been found between the light intensity and the velocity of reaction. For reactions sensitive to a range of frequencies the temperature coefficients appear to increase with increasing wave-length, and are in general less than those of thermal reactions.

The above remarks tend to show that discordant results of experimental attempts to support Einstein's Law should not be regarded as discrediting the law. There is good reason to believe that for a purely photochemical reaction apart from subsidiary complications the law is an exact one.

Mechanism of Reaction.—Following the absorption of a single quantum of radiation by a single molecule, the primary process of a photochemical change is believed to consist, not in the disruption, but the *activation* of the absorbing molecule, which then has the properties of a higher Bohr state; activation is then followed by chemical reaction of the absorbing molecule.[1] It may however happen that the increased energy due to the absorption of a quantum is too small to activate the molecule; hence activation is not a necessary consequence of absorption. It has been shown that the absorption of a quantum greater than the energy required to dissociate the molecule does not always necessarily result in the disruption of the latter, and from such observations together with other theoretical considerations it is now generally accepted that subsequent collision with another molecule is an essential condition for chemical change. Many investigators have regarded the activation of a molecule as a loosening or partial separation of valency electrons, and this view allied with the conception of a rise in quantum state may be taken as the most satisfactory at the present time. The duration of the activated state, before collision, has been calculated and found to vary to some extent according to the class of reaction considered. If, however, no molecular encounter takes place energy will be lost, e.g. as fluorescence, and the original unactivated state be reverted to. It is thought that in certain particular cases a molecule can break up simultaneously as the result of absorption of an energy quantum sufficiently large.[2] In the case of a collision with an inactive molecule the

[1] Stern and Volmer, *Zeitsch. wiss. Photochem.* 1920, **19**, 275.

[2] Franck, *Trans. Faraday Soc.*, March, 1926.

energy of activation is mainly degraded into heat energy ; under conditions more favourable to chemical action there may be a transfer of activation or finally chemical reaction may result. Cases in which the quantum efficiency exceeds unity are found to be invariably exothermic ; activation energy and energy of reaction are liberated which may bring about further decompositions by the suggested formation of *reaction chains* among the atoms present or by a successive activation or rayless transfer of energy. Advancing knowledge of the mechanism and result of light absorption by molecules is likely to clear up many controversial aspects of photochemistry in the course of the next few years.

The Reverse Photo-Electric Phenomenon.—The reverse of the photo-electric effect is the transformation of the kinetic energy of changed particles into light quanta, and under this heading we may include the generation of X-rays themselves. The impact of high-speed electrons (cathode rays) on matter generates light in the form of X-rays which are of high frequency and very short wave-length ; moreover the production of these rays is found to be yet another phenomenon governed by the quantum laws. For the generation of a particular series of X-rays of a certain element forming the anticathode, the kinetic energy E of the impinging electron must exceed a critical value [1] E_1, this produces a light quantum $h\nu$, where ν_1 must not be less than the lowest frequency ν_m of the particular series of rays. The relation found to apply is given by

$$E_1 = \tfrac{1}{2}mv^2 = h\nu_m. \quad . \quad . \quad . \quad . \quad . \quad 111$$

This relation has been confirmed by Webster and Wagner,[2] and using known values of E_1 and ν_m has been used to determine h.

In addition to exciting the characteristic line spectrum of X-rays, the cathode rays also excite a continuous spectrum or impulse radiation, for which also a definite minimum energy E_m of the impinging electron is required for the critical frequency ν_m of the spectrum. The relation here has been shown to be similar to the above :

$$E_m = \tfrac{1}{2}mv^2 = h\nu_m. \quad . \quad . \quad . \quad . \quad . \quad 112$$

and provides a most satisfactory method for the exact determination of h, which is in this way found to be in very close agreement with Planck's value.

[1] Duane and Hunt, *Phys. Rev.* 1915 [ii], **6**, 166 ; Hull, *Phys. Rev.* 1916 [ii], **7**, 157.

[2] *Proc. Amer. Acad.* 1916, **2**, 90 ; *Phys. Rev.* 1916 [ii], **7**, 587 ; *Ann. Physik*, 1915 [iv], **46**, 868.

VIII

ATOMIC HEATS AND THE QUANTUM THEORY

Einstein's Atomic Heat Formula.—Some long-standing problems connected with the atomic heats of chemical elements yielded in a remarkable manner to an application of the Quantum Theory developed by Einstein[1] in 1907. The atomic heat of an element is defined as the product of its atomic weight and its specific heat, or in other words, the amount of heat required to raise a gram-atom (the atomic weight expressed in grams) of the element through one degree of temperature. For poly-atomic substances the molecular heat may be similarly defined by substituting molecular weight for atomic weight and gram-molecule for gram-atom in the above definition.

The thermal content of a monatomic solid may be regarded as the energy of the elastic vibrations of the atoms. For an atom displaced through a distance r the restoring force will be proportional to r and may be written Ar. The potential energy of the displaced atom will be

$$A\int_0^r r.dr = \frac{Ar^2}{2}$$

The kinetic energy is of course given by $\frac{1}{2}mv^2$, and for circular motion about an equilibrium position we must have

$$\frac{mv^2}{r} = Ar \qquad \text{i.e.} \quad \frac{mv^2}{2} = \frac{Ar^2}{2} \quad . \quad . \quad . \quad 113$$

so that the kinetic energy will be equal to the potential energy.

The mean kinetic energy of an atom vibrating in space, i.e. with three degrees of freedom, is from 53 $3kT/2$, hence its mean total energy is $3kT$. One gram-atom of the substance will contain N atoms (N = Avogadro's number) and thus its mean energy U is given by

$$U = 3kNT = 3RT \quad . \quad . \quad . \quad . \quad . \quad 114$$

then for the atomic heat at constant volume we have, taking the value of R as 1·98,

$$C_v = \frac{dU}{dT} = 3R = 5{\cdot}94 \text{ calories per degree} \quad . \quad . \quad 115$$

[1] *Ann. Physik.* 1907 [iv], **22**, 180.

As early as 1819 Dulong and Petit [1] had stated their well-known empirical law, that for a monatomic solid :—Atomic weight $\times$ specific heat, i.e. atomic heat $= 6{\cdot}4$ cals. per degree and is independent of the temperature. Experimental results show that this is simply an average value for the elements, and that a few well-marked exceptions occur. At ordinary temperatures the atomic heats of boron, beryllium, silicon and carbon are much too low, but tend towards the theoretical value at higher temperatures; in the case of diamond, for instance, this is not reached below a temperature of approximately 980° C. Moreover, for the elements generally, the experimental value decreases at low temperatures, tending to zero at the absolute zero of temperature. Although various proposals had been made for dealing with the exceptions, the classical theory afforded no explanation of the variation of the atomic heats with temperature. The explanation involves a departure from the equipartition of energy law, according to which the mean energy of the vibrating atom is given by $3k\mathrm{T}$. From Planck's value $\bar{\mathrm{U}} = h\nu \, \frac{h\nu}{\epsilon^{k\mathrm{T}}} - 1$ for a linearly vibrating atom, if the atom vibrates in space with three degrees of freedom, we get

$$\mathrm{U} = \frac{3h\nu}{\frac{h\nu}{\epsilon^{k\mathrm{T}}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 116$$

For a gram-atom

$$\mathrm{U} = \frac{3\mathrm{N}h\nu}{\frac{h\nu}{\epsilon^{k\mathrm{T}}} - 1} = \frac{3\mathrm{N}k \, . \, \frac{h\nu}{k}}{\frac{h\nu}{\epsilon^{k\mathrm{T}}} - 1} = \frac{3\mathrm{R} \, . \, \frac{h\nu}{k}}{\frac{h\nu}{\epsilon^{k\mathrm{T}}} - 1} \quad . \quad . \quad . \quad 117$$

then

$$\mathrm{C}_v = \frac{d\mathrm{U}}{d\mathrm{T}} = 3\mathrm{R}\left(\frac{h\nu}{k\mathrm{T}}\right)^2 . \frac{\frac{h\nu}{\epsilon^{k\mathrm{T}}}}{\left(\frac{h\nu}{\epsilon^{k\mathrm{T}}} - 1\right)^2} \quad . \quad . \quad . \quad 118$$

This formula corrects the classical constant value 3R by means of a factor which shows that the atomic heat of a monatomic solid is not independent of the temperature, but is a function of $\left(\frac{\nu}{\mathrm{T}}\right)$, and if we assume ν is fixed for a particular solid, the atomic heat is a function of the temperature. If $\mathrm{T} = 0$, i.e. at absolute zero, then $\mathrm{C}_v = 0$, i.e. at absolute zero

[1] *Ann. chim. phys.* 1819, **10**, 395.

the atomic heat itself has fallen to zero ; for high temperatures the value of $\frac{h\nu}{k\mathrm{T}}$ becomes vanishingly small, hence C_v approaches asymptotically the classical value 3R, as experiments show.

Thus once more is seen the beauty and utility of the Quantum Theory in interpreting and generalizing Dulong and Petit's relation, which like Rayleigh's law of radiation is valid only for low frequencies or high temperatures. Einstein's theory of atomic heats was tested by the extensive researches of Nernst and his collaborators.[1] In the case of diamond, experimental values for C_v down to 30° A. show remarkable agreement with the value of C_v calculated from Einstein's equation, but for a large number of other substances the atomic heats at low temperatures fell off much more slowly than is demanded by Einstein's Law.

The Lindemann-Nernst Formula.[2]—Lindemann and Nernst devised a purely empirical formula which gave atomic heat values generally agreeing far more closely with experimental results than the calculations from Einstein's Law. Writing $h\nu/k\mathrm{T} = x$ we may express their relation

$$\mathrm{C}_v = \frac{3\mathrm{R}}{2}\left\{\frac{x^2e^x}{(e^x-1)^2} + \frac{\left(\frac{x}{2}\right)^2 e^{\frac{x}{2}}}{(e^{\frac{x}{2}}-1)^2}\right\} \quad . \quad . \quad . \quad 119$$

Here it is assumed that half of the atoms in the solid vibrate with frequency ν and the other half with frequency $\nu/2$ or an octave lower. This cannot be regarded as the true state of affairs, but it at once suggests to us the probable root of the inaccuracy of Einstein's relation, i.e. in assuming a fixed frequency ν for the atoms of a particular body. Einstein's expression is thus an idealized form, as indeed was recognized by Einstein himself.[3] As against good experimental support for the Lindemann-Nernst formula, there is the serious drawback that it has no sound theoretical basis, whereas Einstein's result was an important progressive step.

Following up the line of reasoning suggested above, it should be necessary, in order to arrive at a perfectly satisfactory ex-

[1] Nernst, Koref and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247 ; 1911, 1912 and 1914, Nernst, *Ann. Physik*, 1911 [iv], **36**, 395. Report to the Solvay Congress at Brussels 1911, *La Théorie du Rayonnement et les Quanta*, 1912, 254, 407.

[2] *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 494.

[3] *Ann. Physik*, 1911 [iv], **35**, 679.

pression, to regard the vibrating atom as possessing a whole spectrum of elastic frequencies corresponding to the overtones of a vibrating string, and to allot to each frequency the theoretical quantum amount of energy $h\nu/e^x - 1$. The problem of calculating this elastic spectrum has been attacked from two points of view. Debye applied the classical theory of elasticity to an elastic continuum as representing a body, and thus neglects crystalline and atomic construction, while Born and Karman [1] considered a space lattice arrangement of the atoms of a body as a crystal of infinite dimensions. The problem is one of extreme difficulty, involving as it does a detailed knowledge of the internal structure and arrangement of the atoms forming the crystal.

Debye's Atomic Heat Formula.—Debye [2] assumes that a vibrating atom cannot vibrate with a single frequency ν, but owing to collisions and mutual action of the atoms, the actual vibration must necessarily be complex. The elastic spectrum of a continuum will consist of a fundamental, and overtones from $\nu = 0$ to $\nu = \infty$; and in the case of a body consisting of N atoms the number of natural frequencies will not be infinite but equal to 3N. Debye overcomes this difficulty by adopting the calculation for a continuum to such a body by taking the natural frequencies between zero and 3N, i.e. by cutting off the elastic spectrum sharply at an upper frequency ν_m related to the atomic dimensions.

For a structureless continuum of volume V the number of vibrations between frequencies ν and $\nu + d\nu$ is given by

$$Z(\nu)d\nu = 4\pi V\left(\frac{1}{c_e^3} + \frac{2}{c_t^3}\right)\nu^2 d\nu \quad . \quad . \quad . \quad . \quad 120$$

where c and c_t are respectively the velocities of propagation for longitudinal and transverse waves. Writing A for the constants in this expression we have

$$Z(\nu)d\nu = A\nu^2 d\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 121$$

Then
$$\int_0^{\nu_m} Z(\nu)d\nu = A\frac{\nu_m^3}{3} = 3N \quad . \quad . \quad . \quad . \quad 122$$

or
$$A = \frac{9N}{\nu_m^3} \text{ so that } Z(\nu)d\nu = \frac{9N}{\nu_m^3}\nu^2 d\nu. \quad . \quad . \quad . \quad 123$$

If we allot to each frequency an amount of energy $h\nu/e^x - 1$

[1] *Phys. Zeitschr.* 1912, **13**, 297; 1913, **14**, 15, 65; *Ann. Physik*, 1914 [iv], **44**, 605; Born, *Dynamik der Kristallgitter* (Teubner, 1915).
[2] *Ann. Physik*, 1912 [iv], **39**, 789.

in accordance with the quantum theory, we have for the total energy of the solid

$$U = \int_0^{\nu_m} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} Z_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad 124$$

$$= k \int_0^{\nu_m} \frac{\frac{h\nu}{k}}{e^{\frac{h\nu}{kT}} - 1} Z_\nu d\nu \quad . \quad . \quad . \quad . \quad . \quad 125$$

Then $$C_v = \frac{dU}{dT} = k \int_0^{\nu_m} \frac{x^2 e^x}{(e^x - 1)^2} Z_\nu d\nu . \quad . \quad . \quad . \quad 126$$

$$= \frac{9Nk}{{\nu_m}^3} \int_0^{\nu_m} \frac{x^2 e^x}{(e^x - 1)^2} \nu^2 d\nu \quad . \quad . \quad . \quad 127$$

Putting $x_m = \frac{h\nu_m}{kT}$ we get ${\nu_m}^3 = \left(\frac{kT}{h}\right)^3 {x_m}^3$; hence $\nu_m = \frac{kT}{h} x_m$ and $d\nu = \frac{kT}{h} dx$.

Substituting in 127

$$C_v = \frac{9R}{{x_m}^3} \int_0^{\nu_m} \frac{\left(\frac{h}{kT}\right)^3 x^2 e^x}{(e^x - 1)^2} \nu^2 d\nu \quad . \quad . \quad . \quad . \quad 128$$

$$= \frac{9R}{{x_m}^3} \int_0^{x_m} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad . \quad . \quad . \quad . \quad . \quad 129$$

which is Debye's formula. Some interesting results follow from this expression; in the first place the atomic heat is clearly a function only of x_m. We can further put $x_m = \frac{h\nu_m}{kT} = \frac{\theta}{T}$; then if we reckon the temperature T as a multiple or submultiple of a temperature θ, where θ is a characteristic constant for a given substance, the atomic heat for all monatomic substances can be represented by the same curve, i.e. the atomic heat is a universal function of θ/T. For high temperatures Debye's formula passes over into Dulong and Petit's value; i.e. if T is large, x_m is small,

then $$\frac{e^x}{(e^x - 1)^2} = \frac{1}{x^2}$$

hence $$C_v = \frac{9R}{{x_m}^3} \int_0^{x_m} \frac{x^4}{x^2} dx = \frac{9R}{{x_m}^3} \cdot \frac{{x_m}^3}{3} = 3R \quad . \quad . \quad . \quad 130$$

On the other hand, for low temperatures, T being small x_m is

large ; replacing x_m in the integral by ∞, the integral becomes an independent constant B :

$$C_v = \frac{9R}{x_m^3}B = 9R.B.\frac{\nu_m^3}{h^3k^3}T^3 = \text{constant} \times T^3 \quad . \quad 131$$

which gives us the fundamental law that at low temperatures the atomic heat is proportional to the third power of the absolute temperature.

Debye's formula has been found to agree satisfactorily with experimental results especially for monatomic elements.[1]

The deduction of the formula, assuming as it does an approximation, cannot be expected to give universally exact results ; it is however the most satisfactory general atomic heat formula in the present state of knowledge of the factors contributing to such a relation. It is especially satisfactory at low temperatures since the amount of energy there concerned is small, in which case only long waves will contribute appreciably to the energy of the body and hence to its atomic heat. Such wave-lengths moreover will be large compared with the distances between atoms, so that the approximation of the body to a continuum is more fully realized.

Atomic Heats of Gases.—Some mention has been made of the distribution of energy among the degrees of freedom of a gas. A monatomic gas will have no energy of vibration ; its energy of translation will be wholly kinetic, and according to the equipartition theory will be divided among three translational degrees of freedom.

$$U = \frac{3}{2}RT \quad . \quad . \quad . \quad . \quad . \quad . \quad 132$$

$$C_v = \frac{dU}{dT} = \frac{3}{2}R = 2{\cdot}98 \text{ calories per molecule} \quad . \quad 133$$

This value has been confirmed by Pier [2] for argon, and has also been shown to be apparently independent of the temperature. A diatomic gas molecule has three translational, one vibrational and two rotational degrees of freedom ; the translational kinetic energy will be $\frac{3}{2}RT$; the rotational kinetic energy will be RT, and there will be equal amounts of potential and kinetic vibrational energy giving RT ; this gives us a total of $\frac{7}{2}R.T.$

[1] Debye, l.c. ; Nernst and Lindemann, *Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 1160.

[2] *Zeitsch. Elektrochem.* 1909, **15**, 546 ; 1910, **16**, 897.

Hence $$U = \frac{7}{2}RT \quad . \quad . \quad . \quad . \quad . \quad . \quad 134$$

and $$C_v = \frac{7}{2}R = 7 \text{ calories approximately} \quad . \quad . \quad 135$$

If, however, vibrational motion is absent, C_v will be reduced to approximately 5 calories. Among the actual values found for C_v are, for hydrogen [1] at 0° C., 4·9 to 5·2 ; at 2000° C., 6·5 ; oxygen and nitrogen, 4·8 and 6·7 at the same respective temperatures ; chlorine, 5·8 at 0° C. and 7 at 1200° C. Evidently the molecular heat of diatomic gases varies considerably with the temperature, and appears to fall off for low temperatures, but the equipartition theory makes no allowance for this variation. Eucken [2] has shown that at low temperatures hydrogen behaves as a monatomic gas, and exhibits no rotational energy, giving $C_v = 2{\cdot}98$ at about 40° absolute. The suggestion therefore arises that this falling off of the rotational energy is a quantum effect, as first suggested by Nernst.[3] The vibrations of the atoms within the molecule correspond to relatively high frequencies and therefore account for a comparatively small proportion of the total energy content of the gas ; the rotational energy, on the other hand, corresponds to low frequencies falling in the infra-red region, and contributing more largely to the total energy. The infra-red absorption spectrum of gases has been discussed by Bjerrum [4] and has received much attention from recent workers. The short, infra-red region absorption bands are generally attributed to atomic vibrations, and the long infra-red region bands to rotations.

Degradation Theory of Gases.[5]—It has been found that in certain cases the molecular heats of gases at very low temperatures fall even below the theoretical value 2·98. This degeneration is regarded by Nernst as due to the substitution of circular rotational motion for translational motion at very low temperatures.

[1] Nernst, *Zeitsch. Elektrochem.* 1911, **17**, 272.
[2] *Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 141.
[3] See note [1].
[4] *Zeitsch. Elektrochem.* 1911, **17**, 731 ; 1912, **18**, 101.
[5] Nernst, *Zeitsch. Elektrochem.* 1914, **20**, 357 ; 1916, **22**, 185 ; Planck, *Sitzungsber. K. Akad. Wiss. Berlin*, 1916, 653.

IX

PLANCK'S SECOND QUANTUM HYPOTHESIS

Dynamics of the Two Hypotheses.—It has been previously remarked in these pages that Planck's revolutionary theory was faced with certain difficulties which ultimately led to the necessity of slight modifications. It is now proposed to deal with this matter in some detail. As regards the Einstein light-quantum hypothesis there is the very greatest difficulty in reconciling it with interference phenomena which receive a clear and natural explanation by the classical undulatory theory. Planck himself, however, does not go to the length of postulating, a quantum-like structure for light and radiation, but confines the quantum conception to the interaction between radiation and matter. The hypothesis of quantum absorption also leads to difficulties. Lorentz [1] has shown that for a weak field of radiation the time required for an oscillator to absorb one quantum of energy is an improbable one. The radiation might conceivably be so weak that the oscillator would be unable to absorb one quantum; moreover, the radiation might be interrupted before a whole quantum had been absorbed.

Planck's relation was deduced on classical grounds which assume continuous energy exchanges, which, although possibly quite true for *average* values of the electrical and magnetic quantities involved, may not necessarily be so for a single oscillator. Further, the photo-electric effect shows no time interval even in cases where, assuming continuous propagation of energy through the ether, the required quantum must need an appreciable time for its absorption. Without making such radical postulates as those of Einstein and Thomson, which involve all the difficulties of interference phenomena on a corpuscular light structure, and lack a sound dynamical basis, Planck [2] decided to meet the difficulties by modifying his theory, and rejected the conception of discontinuous absorption, while retaining that of quantum emission.

His second theory postulates continuous absorption in accord-

[1] *Phys. Zeitschr.* 1910, **11**, 1250.

[2] *Ber. deutsch. physikal. Ges.* 1911, **13**, 138; *Ann. Physik*, 1912 [iv], **37**, 642.

ance with the laws of classical electrodynamics, but discontinuous emission as given by $\varepsilon = h\nu$. Whether an oscillator actually emits when its energy reaches a value represented by an integral number of quanta is defined by a probability law, and between two emissions the energy increases by continuous absorption until it reaches a value again represented by an integral number of quanta. By the first theory $U = n\varepsilon$; but by the second theory, if absorption is continuous then $U = n\varepsilon + \varrho$, where ϱ is a quantity which can vary between zero and ε. For a number of oscillators ϱ will have an *average* value $\varepsilon/2$ or $h\nu/2$, hence we obtain the relation

$$\bar{U} = n\varepsilon + \frac{h\nu}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad 136$$

i.e.

$$\bar{U} = \frac{h\nu}{e^{\frac{h\nu}{k\bar{T}}} - 1} + \frac{h\nu}{2} \quad . \quad . \quad . \quad . \quad . \quad 137$$

Let us consider briefly and compare the dynamics of the first and second hypotheses. Planck employed Gibb's method of specifying the state of an oscillator by means of a state or phase plane, in which the displacement of an oscillator from a position of rest is given by x, and its momentum by y. Every phase point, therefore, corresponds to a momentary condition of an oscillator. Certain states of the oscillator are distinguished by the fact that they form a series of discrete concentric ellipses dividing the phase plane into ring-like strips, all of which possess the same area h ; and, in addition, the energy of the oscillator in one of these states is an integral multiple of $h\nu$. According to Planck's first theory, these special states are the only dynamically possible and stable states of the oscillator, while emission or absorption by the oscillator corresponds to a jump of the phase point from one ellipse to another.

12. Applying the equations of free motion it can be shown that all oscillators having energy ε are represented by points on the ellipse :

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad 138$$

where

$$a^2 = \frac{\varepsilon}{2\pi^2\nu^2 m} \quad . \quad . \quad . \quad . \quad . \quad . \quad 139$$

and

$$b^2 = 2\varepsilon m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 140$$

the area of the ellipse being πab.

The oscillator may be regarded as a point travelling outwards from the origin when its energy is increasing, and inwards when

its energy is decreasing. Maxwell's Law gives us the number of oscillators whose displacements and momenta lie between x and $x + \delta x$ and y and $y + \delta y$ as

$$Ae^{-\frac{\epsilon}{kT}}dx \,.\, dy \quad \ldots\ldots\ldots \quad 141$$

but since this law assumes infinite divisibility of energy among the oscillators it must be modified. Integrating between two ellipses representing energy ε and $\varepsilon + \delta\varepsilon$, the number of oscillators having energies between these limits is

$$N = Ae^{-\frac{\epsilon}{kT}}\frac{\delta\varepsilon}{\nu} \quad \ldots\ldots\ldots \quad 142$$

whereas for infinite divisibility of energy we should have

$$N = \frac{A}{\nu}\int_0^{\infty} e^{-\frac{\epsilon}{kT}}d\varepsilon \quad \ldots\ldots\ldots \quad 143$$

According to Planck the energies of the oscillators can only correspond to the values $\varepsilon_1, \varepsilon_2, \varepsilon_3 \ldots \varepsilon_n$ where $\varepsilon_n = n\varepsilon_1$, and the representative points will lie on, but not between the ellipses corresponding to these. Their motion will be jumps from ellipse to ellipse, and since the elliptic rings have a common area h,

$$\varepsilon_1 = h\nu, \quad \varepsilon_2 = 2h\nu \ldots \varepsilon_n = nh\nu.$$

Then, from the integral in N (above), we have:

$$\begin{aligned} N &= \frac{A}{\nu}\left[e^{-0}\varepsilon_1 + e^{-\frac{\epsilon_1}{KT}}(\varepsilon_2 - \varepsilon_1) + e^{-\frac{\epsilon_2}{KT}}(\varepsilon_3 - \varepsilon_2) + \ldots\right] \\ &= \frac{A}{\nu}\left[h\nu + e^{-\frac{h\nu}{KT}}h\nu + e^{-\frac{2h\nu}{KT}}h\nu + \ldots\ldots\right] \\ &= Ah\left[1 + e^{-\frac{h\nu}{KT}} + e^{-\frac{2h\nu}{KT}} + \ldots\ldots\right] \\ &= Ah\,\frac{1}{1 - e^{-\frac{h\nu}{KT}}} \quad \ldots\ldots\ldots\ldots \quad 144 \end{aligned}$$

Writing the energy for the oscillators represented by the terms of the above series, we have the total energy

$$\begin{aligned} E &= Ah\left[e^{-\frac{h\nu}{KT}}h\nu + e^{-\frac{2h\nu}{KT}}2h\nu + e^{-\frac{3h\nu}{KT}}3h\nu + \ldots\ldots\right] \\ &= Ah^2\nu e^{-\frac{h\nu}{KT}}\left[1 + 2e^{-\frac{h\nu}{KT}} + 3e^{-\frac{2h\nu}{KT}} + \ldots\ldots\right] \\ &= \frac{Ah^2\nu}{\left(1 - e^{-\frac{h\nu}{KT}}\right)^2}\,e^{-\frac{h\nu}{KT}} \quad \ldots\ldots\ldots \quad 145 \end{aligned}$$

Substituting the value found above for N,

$$E = N \frac{h\nu}{1 - e^{-\frac{h\nu}{KT}}} e^{-\frac{h\nu}{KT}}$$

$$= Nh\nu \frac{1}{e^{\frac{h\nu}{KT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad 146$$

$$\bar{U} = \frac{E}{N} = \frac{h\nu}{e^{\frac{h\nu}{KT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 147$$

Hence from 68

$$u_\nu d\nu = \frac{8\pi}{c^3} \cdot \frac{h\nu^3}{e^{\frac{h\nu}{KT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad 148$$

Deduction of the Radiation Law on the First and Second Hypotheses.—Planck's second hypothesis laid the foundations of the most recent developments of the Quantum Theory, and its extension to several degrees of freedom, the following being a brief analysis of the modified views. According to the second theory all points on the phase plane are dynamically possible ; emission, however, takes place in the states represented by the ellipses ; outward motion is continuous, and, following emission at a particular ellipse, the backward motion is a jump. As before

$$N = Ah \frac{1}{1 - e^{-\frac{h\nu}{KT}}} \quad . \quad . \quad . \quad . \quad . \quad 144$$

Substituting for $\bar{U}$ from 137 in $E = N\bar{U}$, we have

$$E = \frac{Nh\nu}{e^{\frac{h\nu}{KT}} - 1} + \frac{Nh\nu}{2} \quad . \quad . \quad . \quad . \quad . \quad 149$$

The number of oscillators whose representative points lie between the nth and $(n + 1)$th ellipses is $Ahe^{-\frac{(n+\frac{1}{2})}{KT}h\nu}$ and the number in the next ring is $Ahe^{-(n+\frac{3}{2})\frac{h\nu}{KT}}$. The ratio of the chance of no emission taking place to the chance of an emission taking place, which by Planck's postulate is proportional to the radiation density, is therefore

$$\frac{e^{-\frac{h\nu}{KT}}}{1 - e^{-\frac{h\nu}{KT}}} = pu_\nu$$

i.e.

$$pu_\nu^4 = \frac{1}{e^{\frac{h\nu}{KT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 150$$

where p is a constant.

Planck now replaces the original relation 68 by

$$\frac{d\bar{U}}{dt} = \frac{\pi e^2}{3m} u_\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 151$$

giving the rate of energy absorption ; from this and the expression for E above

$$ph\nu \frac{d\bar{U}}{dt} = \frac{\pi e^2}{3m} \cdot \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} = \frac{\pi e^2}{3m}\left(\bar{U} - \frac{h\nu}{2}\right) \quad . \quad . \quad 152$$

If ν is s mall, $\frac{h\nu}{kT}$ is small, and $\bar{U}$ tends to the value kT, in which case

$$ph\nu \frac{d\bar{U}}{dt} = \frac{\pi e^2}{3m}\bar{U} \quad . \quad . \quad . \quad . \quad . \quad 153$$

For small values of the frequency ν the energy quanta are so small that emission may be regarded as continuous (cp. the Rayleigh-Jeans deductions), hence we can apply the expression of Hertz [1] for the rate of emission of an oscillator, $\frac{8\pi^2\nu^2e^2}{3c^3m}$ of its own energy ; and equating the rate of emission and absorption for an equilibrium state,

$$\frac{d\bar{U}}{dt} = \frac{8\pi^2\nu^2e^2}{3c^3m}\bar{U} \quad . \quad . \quad . \quad . \quad . \quad . \quad 154$$

from 153 $$ph\nu = \frac{c^3}{8\pi\nu^2}$$

i.e. $$p = \frac{c^3}{8\pi h\nu^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 155$$

so that from 150 we again obtain

$$u_\nu d\nu = \frac{8\pi}{c^3} \cdot \frac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad 148$$

which is identical with 148 from the original arguments. However, according to 137 the mean energy of an oscillator at absolute zero is $h\nu/2$ instead of zero, inasmuch as the oscillators when T = 0 all possess energies between zero and $h\nu$. This is retained since not less than $h\nu$ can be emitted.

The instantaneous photo-electric effect in weak light receives an explanation through Planck's second hypothesis, since a certain number of oscillators will always have an amount of energy infinitesimally smaller than $h\nu$, and from these an elec-

[1] *Wied. Ann.* 1889, **36**, 12.

tron will be ejected practically instantaneously. Unfortunately Planck's second quantum hypothesis appears unable to solve finally the atomic heat problem, neither can specific heat measurements be used to decide between the first and second theories; the reason being that on differentiating the expression for $\bar{U}$ to obtain c_v the additional term $h\nu/2$ disappears.

Planck's Third Modification.—Planck has still further modified his theory [1] by assuming that energy exchange between resonators and radiation is continuous for emission as well as for absorption, but that exchange of energy between resonators and free particles, such as electrons, ions or molecules, takes place in quanta.

The Nernst Heat Theorem.—In the series of experiments undertaken by Nernst and his collaborators,[2] in order to investigate the problem of atomic heats at low temperatures, Nernst obtained support for a conclusion which he had previously arrived at from thermodynamic considerations; that at the absolute zero of temperature the atomic heats themselves tend to the value zero. In its larger significance the matter is connected with heat of chemical reaction and measurement of chemical affinity. The result of Nernst's conclusions is contained in the Nernst Heat Theorem or third law of thermodynamics: For isothermal reactions of a system of solid or liquid bodies at temperature T, in the limiting case when $T = 0$, the maximum work which can be gained from the reaction is independent of the temperature. The following results also follow:

1. In the neighbourhood of absolute zero the atomic heats of such systems remain unchanged during any transformation.

2. At absolute zero all processes proceed without change of entropy.

Planck [3] has extended Nernst's theorem, and concludes that:

1. At absolute zero, the atomic heat vanishes.

2. At absolute zero the entropy of bodies becomes zero.

We may here remark that though Nernst's theorem is itself independent of the Quantum Theory it is found to be in agreement with quantum results. Before passing on to deduce the conclusions stated above it may be permissible to mention very briefly their relation with heat of chemical reaction and chemical affinity.

In 1853 Thomsen proposed that the heat of a reaction or

[1] *Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 918.

[2] *Ann. Physik*, 1911 [iv], **36**, 395; *Sitzungsber. K. Akad. Wiss. Berlin*, 1911 and 1912.

[3] Planck, *Lectures on Thermodynamics.*

diminution of intrinsic energy was a measure of chemical affinity. Berthelot in 1865 embodied a similar conclusion in his law of maximum work :—If A is the work done on a system and U is the increase of energy of the system, then A = U. This result is not found to be generally satisfactory, as numerous exceptions are known. Helmholtz in 1882 gave the correct relation that chemical affinity is measured by the diminution of *free* energy, or minimum work of the reaction, i.e.

$$A = U + T\frac{dA}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad 156$$

Now at absolute zero $T = 0$, hence $T\frac{dA}{dT} = 0$, so that $A = U$,

that is, round about absolute zero the maximum work obtainable is independent of the temperature. Nernst's theorem can thus be stated in the form :—For limit $T = 0$

$$\frac{dA}{dT} = 0 \qquad \frac{dU}{dT} = 0 \quad . \quad . \quad . \quad . \quad . \quad 157$$

Deduction of the Radiation Law.—Let us apply the laws of thermodynamics to the change of a system from a condition of initial energy U_1 to final energy U_2.

The first law of thermodynamics give us

$$dU = dA + dQ \quad . \quad . \quad . \quad . \quad . \quad 158$$

where A is the work done *on* the system, and U the increase in energy of the system ; the second law of thermodynamics gives

$$dS = \frac{dQ}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad 159$$

Denoting the free energy by F,

$$F = U - TS \quad . \quad . \quad . \quad . \quad . \quad . \quad 160$$

i.e.
$$\begin{aligned} dF &= dU - TdS - SdT \\ &= (dA + dQ) - TdS - SdT \\ &= dA + TdS - TdS - SdT \quad . \quad . \text{ from } 159 \end{aligned}$$

$$= -dA - SdT \quad . \quad . \quad . \quad . \quad . \quad 161$$

For an isothermal process $dT = 0$ and hence $dF = dA$.

If A' = work gained, i.e. $A' = -A$,
then for a finite change $F_2 - F_1 = A = -A'$
i.e. $F_1 - F_2 = A'$

that is, the work gained in an isothermal reversible reaction is equal to the decrease of free energy.

At constant volume V, $dA = 0$; hence

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{from 160}$$

i.e. $$T\left(\frac{\partial F}{\partial T}\right)_V = -TS = F - U \quad \text{from 161}$$

for two states

$$T\left[\frac{\partial(F_1 - F_2)}{\partial T}\right]_V = (F_1 - F_2) - (U_1 - U_2) = A' - U' \quad .162$$

i.e. $$T\frac{dA}{dT} = A' - U' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 163$$

This is the important relation known as the maximum work equation. According to Nernst, if $T = 0$, then $A' - U' = 0$ and $\partial U'/dT = 0$, or

$$\frac{\partial U_1}{\partial T} = \frac{\partial U_2}{\partial T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 164$$

but dU/dT for a gram atom is the atomic heat; thus we have deduced from Nernst's theorem with the help of thermodynamics that at the absolute zero the atomic heat is unchanged during any transformation.

Again, we have seen $\dfrac{\partial F}{\partial T} = -S$.

Hence $$\frac{\partial(F_1 - F_2)}{\partial T} = S_2 - S_1$$

i.e. $$S_2 - S_1 = \frac{\partial A'}{\partial T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 165$$

which, when $T = 0$, gives us $S_2 - S_1 = 0$, or at absolute zero all processes proceed without change of entropy.

Planck's Extension of Nernst's Theorem.—According to this extension, at absolute zero not only do the differences of entropy become zero, but the entropies themselves are equal to zero. For from 160 $F - U = -TS$, and by Planck's view $F - U = 0$ when $T = 0$; hence

$$\frac{\partial(F - U)}{\partial T} = 0 \quad \text{i.e.} \quad -S - \frac{\partial U}{\partial T} = 0$$

i.e. $$\frac{\partial U}{\partial T} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 166$$

that is, at absolute zero the atomic heat of a body vanishes.

Planck's extension, though not dependent on the Quantum Theory, is in agreement with it inasmuch as from both lines of argument atomic heats vanish at absolute zero.

Thermodynamics and Ionization.—Laue and Tolman have shown that free electricity in a gaseous phase should have the properties of a monatomic gas, and Saha has calculated the ionization as a function of the temperature by assuming that gaseous electrons obey the same entropy law as other monatomic gases. The term U in the general free energy equation is assumed to be measured by the ionization potential, and this equation and the entropy equation have been applied to metallic vapours ionized at low pressures.

X

THE QUANTUM THEORY OF OPTICAL SPECTRA

The Rutherford-Bohr Atomic Model.—A brilliant triumph was achieved by the Danish physicist Niels Bohr in 1913 by the application of the Quantum Theory to Rutherford's atomic model. Briefly, it may be said that Bohr was able to define the orbits in which an electron might travel round the atomic nucleus, and the conditions under which the electron might cause the emission of light giving rise to spectral lines of definite frequency. The Balmer series of hydrogen lines, the spectrum of helium and the Rydberg constant were among some important points which found a natural and satisfactory interpretation in the new scheme. We will now consider Rutherford's atom and the development of Bohr's work. Since the discovery of the electron by Crooke's experiments on the discharge tube, an immense amount of work had been done on the problem of evolving a satisfactory model of the atom. Among the most important was the one proposed by Rutherford [1] in 1911, and suggested by his experimental work on the scattering of α particles in their passage through matter. According to Rutherford's view the atom consists of a minute central nucleus carrying a net positive charge and accounting for practically the whole mass of the atom; while around this nucleus, and concentric with it, electrons circulate in a series of planetary orbits. The outermost ring is considered to contain the so-called valency electrons, which are most easily removed, while as we progress inwards the energy corresponding to each orbit increases, making removal of electrons more difficult, until for the innermost ring the ejection of an electron requires the high energy of a cathode ray. The return of this electron gives rise to a very short wave known as an X-ray, the shortest wave-length which the atom is capable of emitting.

In the electrically neutral atom, the number of planetary electrons corresponds to the atomic number of the element, the function of the nucleus being to provide the mass of the atom and to hold together the electron rings. The field strength of the nucleus increases up to its immediate neighbourhood in accordance with Coulomb's inverse square law, which would

[1] *Phil. Mag.* 1911 [vi], **21**, 669.

account for the large deflection of α particles passing close to the nucleus. It is practically certain also that the nucleus contains a certain number of firmly bound electrons which are the source of the β particles of radioactive substances.

On closer inspection, however, the Rutherford atom is incapable of fulfilling a most necessary condition of an atomic model: the emission of a definite homogenous spectral line characteristic of the particular atom. On classical mechanics the motion of a charged particle (the electron) rotating in a closed orbit is continuously accelerated towards the centre, hence the electron must be continuously emitting radiation. In so doing it must be losing energy and therefore its orbit must be decreasing until finally the electron falls into the nucleus. Now the spectrum of an atom is a definite characteristic of that atom, but energy radiation such as the above involves a continuous alteration in wave-length of the emitted radiation.

Bohr's Hypothesis.—The difficulty was overcome by Bohr,[1] who applied certain hypotheses to this model.

I. Contrary to classical mechanics the possible orbits of the electrons are not unrestricted, but are determined in accordance with the quantum principle, only those paths being permissible for which the moment of momentum [2] (turning impulse, or angular momentum) is an integral multiple of $h/2\pi$.

II. These orbits are to be regarded as stable states of motion, in the sense that the electron shall not radiate in a quantum orbit.

III. An electron can pass from one orbit to another in a jump, and may not have an intermediate position. If the electron falls from an outer to an inner orbit it loses energy which is emitted in the form of radiation; e.g. if the electron falls from a quantum orbit (stationary state) corresponding to energy W_2 into an inner orbit corresponding to energy W_1, an amount of energy equal to $W_2 - W_1$ must be radiated, and this will be for adjacent orbits an energy quantum $h\nu$, hence the frequency of the emitted radiation will be given by the relation

[1] *Phil. Mag.* 1913, **26**, 476, 857; 1914, **27**, 506; 1915, **30**, 394; Bohr, *The Theory of Spectra and Atomic Constitution* (Camb. Univ. Press).

[2] Moment of momentum. The angular momentum of an electron is its mass multiplied by its velocity in a curved path. If r is the radius of the orbit, v the velocity of the electron, and ν its rotation frequency,

$$\begin{aligned} \text{Angular velocity } \omega &= 2\pi\nu \\ v = r\omega &= 2\pi r\nu \\ \text{Moment of momentum} &= mvr \\ &= mr^2\omega \\ &= 2\pi mr^2\nu \end{aligned}$$

$$\nu = \frac{W_2 - W_1}{h} \quad . \quad . \quad . \quad . \quad . \quad . \quad 167$$

IV. Classical dynamics are applicable to the equilibrium of an electron in the stationary states, i.e. the centrifugal force due to the speed of revolution of the electron is balanced by the electrostatic attraction of the positive nucleus.

The hypothesis of stationary states is in agreement with the theory that the magnetism of iron is due to revolving electrons, which can revolve in atoms without emitting energy of radiation.

The Balmer Series.—We will next consider some relations found for spectral line series, and then proceed to show their interpretation by Bohr's hypothesis.

As long ago as 1885 Balmer discovered a simple empirical expression for the lines in the spectrum of hydrogen :

$$\text{Wave number} = \frac{10^8}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad 168$$

where n denotes successive integers 3, 4, 5, etc.

R is here not to be confused with the gas constant, but denotes the Rydberg constant. This is a vibration frequency which was found by the Swedish physicist Rydberg to occur in expressions for the spectral lines of a number of elements. Its value can be calculated from the relation for hydrogen above and may be taken as 109,675. The wave number denotes the number of waves per centimetre. For frequency $\nu = c/\lambda$ the value of R is given by

$$\nu = \text{wave number} \times c = \frac{c10^8}{\lambda} = 3 \times 10^{10} \times 109{,}675\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$$= 3{\cdot}290 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad . \quad 169$$

Rydberg showed that, apart from the simple spectrum of hydrogen, the spectrum of many elements contains series of lines whose wave-length is given approximately by

$$\frac{1}{\lambda} = A - \frac{R}{(n - a^2)} \quad . \quad . \quad . \quad . \quad . \quad 170$$

where A and a are constants having different values for the various series.

The Combination Principle.[1]—The relations between the constants in the various series for an element were generalized by Ritz in the combination principle, according to which the

[1] Ritz, *Phys. Zeitschr.* 1908, **9**, 521.

wave-lengths of the various lines in the spectrum are given by

$$\frac{1}{\lambda} = \mathrm{F}_r(n_1) - \mathrm{F}_s(n_2) \quad . \quad . \quad . \quad . \quad . \quad 171$$

in which n_1 and n_2 are integers, and $\mathrm{F}_1(n)$, $\mathrm{F}_2(n)$ is a series of functions of n which may be written

$$\mathrm{F}_r(n) = \frac{\mathrm{R}}{(n + a_r)^2} \quad . \quad . \quad . \quad . \quad . \quad 172$$

where a_r is a constant differing for the various functions. This principle gives us a means of obtaining the entire spectrum by forming the possible combinations of two values of $\mathrm{F}(n)$, keeping one constant at a time. This allowed the prediction of a large number of spectral lines, confirmed by subsequent discovery and in agreement with the calculations.

The ordinary laboratory spectrum of hydrogen reveals 12 lines, the strongest of which lies at the red end of the spectrum, while the others, diminishing in intensity and in distance apart, converge to a limit in the ultra-violet. Ritz generalization gives for hydrogen a series of the type

$$\nu = \mathrm{R}\left(\frac{1}{{n_1}^2} - \frac{1}{{n_2}^2}\right). \quad . \quad . \quad . \quad . \quad . \quad 173$$

which leads us to expect an infra-red series given by

$$\nu = \mathrm{R}\left(\frac{1}{3^2} - \frac{1}{n^2}\right). \quad . \quad . \quad . \quad . \quad . \quad 174$$

the first two lines of this series ($n = 4, 5$) were observed by Paschen [1] in 1908, and the next three ($n = 6, 7, 8$) by Brackett [2] in 1922. This series is known as the Bergmann or Paschen series. Again, if we put $n_1 = 1$ and $n_2 = 2, 3, 4$, we have the ultra-violet series subsequently discovered by Lyman [3] in 1914.

Mathematical Treatment of Bohr's Theory.—Bohr considers in the first instance the simplest atom, hydrogen. This, according to the Rutherford model, consists of a central positive nucleus and one electron rotating in an orbit about it. The mass of the electron may here be regarded as negligible compared with that of the nucleus, and the orbit circular. Let e be the electron charge, E the nuclear charge and m the mass of the electron. In general $\mathrm{E} = ez$, where z is the atomic number. For hydrogen $z = 1$, hence $\mathrm{E} = e$. Also let r be the radius of

[1] *Ann. Physik*, 1908 [iv], **27**, 565.
[2] *Nature*, 1922, **109**, 209.
[3] *Nature*, 1914, **93**, 241; *Phil. Mag.* 1915 [vi], **29**, 284.

the orbit, v the velocity of the electron, and ν its frequency of rotation. Its angular velocity ω is, as we have seen, $2\pi\nu$. The attractive force of the nucleus on the electron is $\mathrm{E}e/r^2$; then, according to Newtonian mechanics, the condition for a circular orbit is

$$\frac{\mathrm{E}e}{r^2} = \frac{mv^2}{r} = \frac{mr^2\omega^2}{r} = mr\omega^2 \quad . \quad . \quad . \quad . \quad 175$$

from which $v^2 = \dfrac{\mathrm{E}e}{mr}$ where r can have any value.

The kinetic energy of the electron is $\frac{1}{2}mv^2$, which from 175 is $\dfrac{1}{2}\dfrac{\mathrm{E}e}{r}$. Let W denote the work required to remove the electron from its orbit to infinity, i.e. to ionize the atom, then

$$\mathrm{W} = \tfrac{1}{2}mv^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 176$$

Bohr assumes that we must have

$$\mathrm{W} = \tfrac{1}{2}nh\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 177$$

Relating this to the moment of momentum $2\pi mr^2\nu$ or $\dfrac{\mathrm{W}}{\pi\nu}$ we have

$$\frac{\mathrm{W}}{\pi\nu} = \frac{1}{2} \cdot \frac{nh\nu}{\pi\nu}$$

$$= n \cdot \frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad 178$$

Bohr thus limits the number of orbits, only those being permissible for which the moment of momentum is an integral multiple n of $\dfrac{h}{2\pi}$,

i.e.
$$mr^2\omega = n\frac{h}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 179$$

From this equation

$$r^4 = \frac{n^2h^2}{4\pi^2m^2\omega^2}$$

From 175
$$r^3 = \frac{\mathrm{E}e}{m\omega^2}$$

Dividing,
$$r_n = \frac{n^2h^2}{4\pi^2m\mathrm{E}e} \quad . \quad . \quad . \quad . \quad . \quad . \quad 180$$

By giving successive integral values to n ($n = 1, 2, 3$) this relation gives us a definite series of orbits with radii proportional to n^2.

Obtaining the corresponding series of velocities from 179

$$mr^2\omega = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 179$$

$$\omega = \frac{nh}{2\pi mr^2}$$

$$= \frac{nh}{2\pi m} \cdot \frac{16\pi^4 m^2 \mathrm{E}^2 e^2}{n^4 h^4}$$

$$= \frac{8\pi^3 m \mathrm{E}^2 e^2}{n^3 h^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 181$$

or since $\omega = \frac{v}{r}$

$$v = \frac{2\pi \mathrm{E}e}{nh} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 182$$

The velocities are therefore proportional to $\frac{1}{n}$.

Finally, to obtain an expression for the energy of the quantum orbits :

$$\mathrm{W} = \frac{1}{2} m v^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 176$$

$$= \frac{1}{2} m \cdot \frac{4\pi^2 \mathrm{E}^2 e^2}{n^2 h^2}$$

$$= \frac{2\pi^2 \mathrm{E}^2 e^2 m}{n^2 h^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 183$$

Now, according to 167, the energy loss in the fall of an electron from an orbit n_2 to an orbit n_1 is given by

$$h\nu = \mathrm{W}_2 - \mathrm{W}_1$$

i.e. $$\nu = \frac{\mathrm{W}_2 - \mathrm{W}_1}{h} = \frac{2\pi^2 \mathrm{E}^2 e^2 m}{h^3}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \quad . \quad . \quad 184$$

Bohr supposes that this liberated energy passes into space in the form of monochromatic radiation and amounts to exactly one quantum, hence the frequency of the emitted light is given by the above relation. For a jump between two stationary states n_1 and n_2 this represents only a single line, while, as we know, there are in reality a number of lines in the spectrum of an element. But a number of stationary states are possible, represented by giving a series of integral values to n ; thus the general series of spectral lines is accounted for. As will be seen by reference to 183, the value of W is greatest when n is lowest, i.e. unity ; this, therefore, corresponds to the most stable state of the atom.

The Hydrogen Spectrum.—If we put $E = e$ and $n_2 = 2$, we obtain a series of spectral lines whose frequencies are given by

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \text{ where } (n = 3,\ 4,\ 5\ \ldots). \quad 185$$

We should expect the term $2\pi^2 me^4/h^3$ to represent R the Rydberg constant, and thus we obtain the Balmer series. This series then, according to Bohr's theory, is emitted when an electron falls from the 3rd, 4th, 5th . . . quantum orbit to the second orbit.

Let us substitute numerical values for the constants

$$e = 4{\cdot}774 \times 10^{-10} \text{ e.s. units.}$$
$$m = 9{\cdot}00 \times 10^{-28} \text{ gm.}$$
$$h = 6{\cdot}55 \times 10^{-27} \text{ erg/sec.}$$

then $\dfrac{2\pi^2 me^4}{h^3} = \mathrm{R} = 3{\cdot}294 \times 10^{15}$, which is in remarkably good agreement with the value of R previously found on experimental data.

For the radius of the innermost orbit $n = 1$ we have from 180

$$r_1 = {\cdot}53 \times 10^{-8} \text{ cm.}$$

and

$$r_2 = 2{\cdot}12 \times 10^{-8} \text{ cm.}$$

from 182

$$v_1 = 2{\cdot}19 \times 10^{8} \text{ cm./sec.}$$

or about 150 times less than the velocity of light. The rotational frequency per second gives us

$$\nu = \frac{v}{2\pi r} = 6{\cdot}6 \times 10^{15}$$

The above results are of the accepted order of magnitude for the various values as obtained by other methods.

If we put $n_2 = 1$ in Bohr's formula we obtain

$$\nu = \mathrm{R}\left(1 - \frac{1}{n^2}\right) \text{ where } n = 2,\ 3,\ 4,$$

the Lyman ultra-violet series. Finally putting $n_2 = 3$ we have

$$\nu = \mathrm{R}\left(\frac{1}{3^2} - \frac{1}{n^2}\right) \text{ where } n = 4,\ 5,\ 6,$$

the Paschen infra-red series.

It has been remarked that only twelve lines of the Balmer series are ordinarily observed in laboratory vacuum discharge tubes, while 33 lines have been observed in certain stellar spectra, and 29 lines have been identified in the spectrum of the solar chromosphere. The 12th line would be emitted by an electron jumping from the 14th to the 2nd orbit, i.e. $n_2 = 14$, $n_1 = 2$, from which the 14th orbit radius can be shown to be $0{\cdot}8 \times 10^{-6}$ cm.,

which corresponds to the mean distance apart of the molecules of a gas at a pressure of about 7 mm. of mercury. The 29th line, for which $n_2 = 31$, involves an atomic diameter of about $1{\cdot}02 \times 10^{-5}$ cm., or nearly one thousand times that of the normal hydrogen atom. The possibility of such inflated atoms might be allowed in view of the extremely low pressure existing in the atmosphere of celestial bodies, hence the experimental detection of so large a number of lines necessitates a very low pressure and a correspondingly small gas density, but in the extreme cases so little gas would then be present in the vacuum tube that the intensity of emission would be too faint to be detected. In

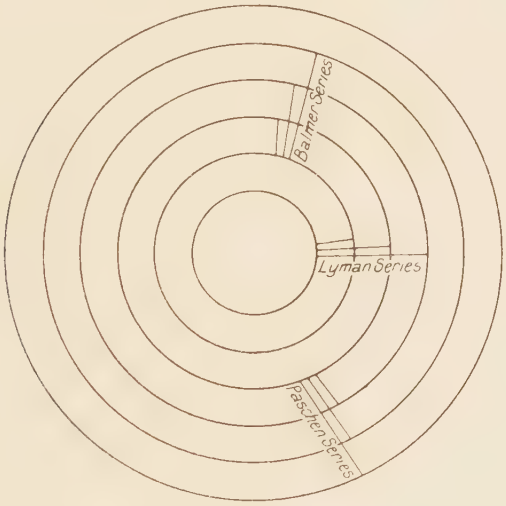

FIG. 5.

the solar atmosphere, however, the large mass of highly rarefied incandescent gas affords favourable conditions for observation of higher lines. In some recent experiments by R. W. Wood,[1] the Balmer series was observed down to the twentieth line, but as the pressure was gradually raised the higher lines of the series disappeared successively, in accordance with the above views. We can represent the electron jumps giving rise to the first three lines of the Balmer, Lyman and Paschen series in a diagram (Fig. 5), which illustrates clearly the explanation which has been given of these lines.

Bohr himself points out that his theory makes no pretence of *explaining* the spectral laws, or how and why radiation is emitted,

[1] *Proc. Roy. Soc.* 1920, **97A**, 455.

Rather it attempts to show that certain features of atomic structure are incapable of being explained on classical grounds, and that the energy problem involved is, as in the case of temperature radiation, in conformity with Planck's theory of energy transfer in quanta. The treatment of the origin of the hydrogen spectrum leads us to interpret this spectrum as a manifestation of the process whereby the electron is bound to the nucleus, and throws light on the formation of the hydrogen atom, since the stationary states may be regarded as different stages of a process by which the electron, under the emission of radiation, is bound in orbits of decreasing dimensions.

The final stage of the binding process leads to a stationary state in which $n = 1$, which corresponds to the minimum energy of the atom and a maximum value of W, i.e. the work required to ionize the atom. This may be termed the "normal state" of the atom.

An interesting result is reached by considering a negatively charged hydrogen atom, or one which has picked up an extra electron. In this case $e = 2$, and on calculating the corresponding value of W, the latter is found to be greater than the value for a neutral atom, which agrees with the fact that the hydrogen atom can take on such an extra charge, as is supported by certain of the chemical reactions of the element. If, however, we calculate W for the case in which $e = 3$, i.e. the addition of two extra electrons, the value of W is less than for the neutral atom, from which we conclude that such an atom would be unstable, and this is also in agreement with experimental evidence.

The Helium Spectrum.—The element helium follows hydrogen in the periodic table, its atomic number being 2, and the atom, according to Rutherford's model, consisting of a doubly charged nucleus, $E = 2e$, and two electrons revolving round it in different orbits. In the case of the ionized helium atom, one of these has been removed.

In 1897 Pickering observed in a stellar spectrum a series of lines showing some analogy to that of hydrogen, and which could be represented to a close approximation by the formula

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{(n + \frac{1}{2})^2}\right) \quad . \quad . \quad . \quad . \quad 186$$

These were attributed to hydrogen, and Rydberg predicted a further series of the type

$$\frac{1}{\lambda} = R\left(\frac{1}{(\frac{3}{2})^2} - \frac{1}{n^2}\right) \quad . \quad . \quad . \quad . \quad . \quad 187$$

of which one line corresponding to $n = 2$ was actually observed.

Bohr, however, showed that the Pickering lines could be explained by assuming that they were due to a single electron revolving round a doubly charged nucleus, or in other words that they were due to ionized helium. That they were not observed in the laboratory was probably due to the high degree of ionization required; but in 1912 Fowler,[1] by passing a very heavy current through a mixture of hydrogen and helium, observed not only these lines but also a new series given approximately by

$$\frac{1}{\lambda} = \mathrm{R}\left(\frac{1}{(\frac{3}{2})^2} + \frac{1}{(n+\frac{1}{2})^2}\right) \quad . \quad . \quad . \quad . \quad 188$$

Now let us apply Bohr's theory to the ionized helium atom. If we put $\mathrm{E} = 2e$ we obtain

$$\nu = \frac{2\pi^2 e^4 m}{h^3} \cdot 4\left(\frac{1}{{n_2}^2} - \frac{1}{{n_1}^2}\right) \quad . \quad . \quad . \quad . \quad 198$$

$$= 4\mathrm{R}\left(\frac{1}{{n_2}^2} - \frac{1}{{n_1}^2}\right)$$

$$= \mathrm{R}\left(\frac{1}{\left(\frac{n_2}{2}\right)^2} - \frac{1}{\left(\frac{n_1}{2}\right)^2}\right) \quad . \quad . \quad . \quad . \quad 189$$

Putting $n_2 = 4$ and $n_1 = 5, 6, 7 \ldots$ the even integrals n_1 give us the Balmer series, which can therefore be emitted by helium as well as by hydrogen, while the odd integrals n_1 give us the Pickering series.

If $n_2 = 3$ and $n_1 = 4, 5, 6 \ldots$ the even integrals n_1 give us the series predicted by Rydberg, and the odd integrals n_1 give us the new series 188 observed by Fowler. These latter series have been confirmed by Evans,[2] and measured by Paschen[3] in tubes from which all hydrogen had been removed, and in which no traces of known hydrogen lines could be obtained.

The Rydberg Constant.—In the previous discussions we have neglected the mass of the electron compared to that of the nucleus, and also the motion of the nucleus relative to the electron. Actually the nucleus and electron will revolve about their common centre of gravity. Even if we neglect this, and assume that the common centre of gravity coincides with the nucleus, the error involved is very small, since the order of mass of the nucleus and the electron is approximately in the ratio

[1] *Monthly Notices Roy. Astron. Soc.* 1912, 62; *Phil. Trans.* 1914, 214A, 254.

[2] *Phil. Mag.* 1915 [vi], **29**, 284.

[3] *Ann. Physik*, 1916 [iv], **50**, 901.

1800 to one, so that the common centre of mass lies extremely close to the nucleus and hence the relative motion of the latter will be correspondingly small.

On making the necessary correction [1] the value of the Rydberg constant is found to be given by

$$R = \frac{2\pi^2 e^2 E^2 m}{h^3} \frac{M}{M+m} \quad . \quad . \quad . \quad . \quad . \quad 190$$

where M is the mass of the nucleus. Now since the mass of the helium nucleus is slightly greater than that of the hydrogen nucleus, the Rydberg constant will be slightly larger for helium than for hydrogen, and from analogy we should expect the value of the Rydberg constant to increase for the other elements with their atomic weight, to a limiting value. This, again, is in agreement with spectroscopic results. By such means Fowler [2] has obtained for the ratio $\frac{M}{m}$, in the case of hydrogen, the value 1836.

A further correction has been made by Paschen,[3] who, taking account of a necessary relativity correction and other details, obtained the value 1843·7, which is in striking agreement with 1845, the best value obtained by Millikan.

Generalized Equation for the Bohr Atom.—Bohr's hypothesis has given us, for an atom consisting of a nucleus and one electron, the equation for the kinetic energy T:

$$T = W = \tfrac{1}{2}nh\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 177$$

and in connection with the specific heats of solids at low temperatures we have had for the energy of wave vibration E in an elastic solid

$$E = nh\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 191$$

In the first equation the kinetic energy of the revolving electron is wholly kinetic, while in the second

$$\bar{T} = \bar{V} = \tfrac{1}{2}E \quad . \quad . \quad . \quad . \quad . \quad . \quad 192$$

where $\bar{T}$ and $\bar{V}$ represent the average value of the kinetic and potential energies respectively over a complete period.

Since in 177 T is constant throughout the motion, we can write

$$2T = 2\bar{T} = nh\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 193$$

while 191 and 192 give us

$$2\bar{T} = nh\nu \quad . \quad . \quad . \quad . \quad . \quad . \quad 194$$

[1] Bohr, *Phil. Mag.* 1914 [vi], **27**, 506.
[2] Bakerian Lecture, *Phil. Trans.* 1914, **214**A, 225.
[3] *Ann Physik*, 1916 [iv], **50**, 901.

Hence 171 and 191 are now covered by the general equation 194, which can also be written

$$\frac{2\bar{T}}{\nu} = nh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 195$$

Now the quantity $2\bar{T}/\nu$ is what is known as an "adiabatic invariant."[1] This may be explained as follows: if such a quantity denoted by F defines the motion of a dynamical system according to the equation

$$F = nh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 196$$

then F must be such that when the parameters which specify the strength or condition of an external field of force acting on the system gradually change, F shall remain unchanged in value.

Sommerfeld's Theory of the Fine Structure of Spectral Lines.—An important development of Bohr's theory of spectra was effected in 1915 by Planck [2] and Sommerfeld.[3] As we have seen, Bohr's circular orbits are determined by a single quantum condition; the new development extended the number of possible orbits by taking account of Kepler ellipses. In this case the electron path is determined by two quantum conditions, since two parameters are required to define elliptic motion, the condition with regard to the size of the orbit being given by the major axis of the ellipse, and with regard to its form, given by the mutual relation of the axes. The two conditions may be expressed in the form

$$\int_0^{2\pi} p_1 d\theta = n_1 h \quad . \quad . \quad . \quad . \quad . \quad 197$$

$$\int p_2 dr = n_2 h. \quad . \quad . \quad . \quad . \quad . \quad . \quad 198$$

p_1 and p_2 are the momenta corresponding to polar co-ordinates θ and r, the second integral being taken over a full range of r, while n_1 and n_2 are the two quantum numbers. The method by which 197 and 198 are derived is such as to provide a solution to the problem of the extension of the Quantum Theory to several degrees of freedom; the above case being an extension

[1] Boltzmann, 1876, *Vorlesungen über Mechanik*, II, § 48; Ehrenfest, *K. Akad. Wetensch.* Amsterdam, 1916, **25**, 412; Bohr, "On the Quantum Theory of Line Spectra," *Kgl. Danske Selsk. Skrifter, Naturvidoog Mathemat.* 1918, **4**, 10.

[2] *Ber. deutsch. physikal. Ges.* 1915, **17**, 407, 438; *Ann. Physik*, 1916 [iv], **50**, 385.

[3] *Ann. Physik*, 1916 [iv], **51**, 1.

to two degrees of freedom. The left-hand members of these equations are known to be adiabatic invariants.

Let us apply this new extension to Bohr's atomic model. We now have as permissible orbits, in place of Bohr's quantized circles, quantized Kepler ellipses, among which Bohr's circles are included as special cases. The hydrogen-type series formula now becomes

$$\nu = \mathrm{R}\left[\frac{1}{(n_1 + n_1')^2} - \frac{1}{(n_2 + n_2')^2}\right] \quad . \quad . \quad 199$$

This indicates that the frequency of the emitted line depends on the sum $(n_1 + n_1')$ and $(n_2 + n_2')$ and not on the individual values of n_1, n_1', n_2 and n_2'.

Bohr's theory interprets the first line of the Balmer series as being caused by an electron falling from the orbit $n = 3$ to the orbit $n = 2$; or in terms of the above relation, from an orbit $n_1 = 3$; $n_1' = 0$ to $n_2 = 2$; $n_2' = 0$. Now according to Sommerfeld's extension this same line can be emitted under the following possible conditions in each of which $(n_1 + n_1') = 3$ and $(n_2 + n_2') = 2$.

n_1	n_1'	n_2	n_2'
3	0	2	0
2	1	1	1
1	2	2	0
3	0	1	1
2	1	2	0
1	2	1	1

The values $n_1 = 0$; $n_1' = 3$ and $n_2 = 0$; $n_2' = 2$ are probably impossible, since they would require the electron to pass through the nucleus. Sommerfeld's work thus indicates a much larger number of possible orbits, from which it follows that the electrons have a greater number of chances of passing from one orbit to another, and hence the possibility of the emission of a certain spectral line is greatly increased, *but no new line is to be expected.*

The single Bohr line must accordingly be regarded as identical with six exactly coincident lines emitted by six electronic jumps specified in the table. At first sight, therefore, the more complicated theory of elliptic motion appears to possess no very important advantage over Bohr's circles. A definite spectral line is not however a true mathematical line, corresponding to a definite frequency. The hydrogen spectral lines, viewed under high dispersion, were known to exhibit doublets, i.e. the individual lines appeared as groups of two lines extremely close together.

The utility of Sommerfeld's extension becomes apparent when we introduce a relativity correction for the mass of the electron. If m_0 is the ordinary mass, then m the mass of the particle corrected for velocity is given by

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad . \quad . \quad . \quad . \quad . \quad 200$$

For all ordinary velocities the quantity v^2/c^2 is negligible, making the denominator of the fraction unity, and is only of importance when v is comparable with c the velocity of light. As the speed of the electron cannot be regarded as negligible in comparison with that of light, the small correction for consequent change of mass is necessary. Sommerfeld introduced the required correction, and found that an electron orbit was now given by a steadily advancing ellipse, or that the perihelion of the orbit advances in the course of time. He also showed that the energy of the electron in the stationary quantum orbits is no longer independent of the sum of the individual values of n_1; n_1', etc., given in 199. The introduction of the relativity correction means that the energy value W and the frequency are influenced by the actual values of the components of the quantum numbers. The finally corrected values of W and ν are given by the expressions

$$\mathrm{W} = \frac{2\pi^2 m_0 e^2 \mathrm{E}^2}{(n_1 + n_1')^2 h^2}\left[1 + \left(\frac{2\pi e \mathrm{E}}{hc(n_1 + n_1')}\right)^2 \left(\tfrac{1}{4} + \frac{n_1'}{n_1}\right)\right] \quad 201$$

$$\nu = \frac{2\pi m_0 e^2 \mathrm{E}^2}{h^3}\left\{\frac{1}{(n_1 + n_1')^2} - \frac{1}{(n_2 + n_2')^2}\right\}$$
$$\left[1 + \left(\frac{2\pi e \mathrm{E}}{hc}\right)^2 \tfrac{1}{4}\left(\frac{n_1'}{n_1} - \frac{n_2'}{n_2}\right)\right]. \quad 202$$

The generation of a spectral line is thus shown to depend not on the sum $(n_1 + n_1')$ and $(n_2 + n_2')$ alone, but that variations in the two terms making up the quantum numbers represented by the whole bracket give rise to slightly different lines lying very close together. Sommerfeld's brilliant theory of the fine structure of spectral lines has been confirmed experimentally by the observations, among others, of Paschen [1] for ionized helium and of Michelson, Fabry and Buisson, Merton and Nicholson and McLennan and Shrum for hydrogen.[2]

[1] *Ann. Physik*, 1916 [iv], **50**, 901.
[2] *Nature*, 1923, **112**, 166.

Röntgen Spectra.—The generation of Röntgen rays in a Röntgen ray tube in general gives rise to an impulse radiation or a continuous range of wave-lengths, and a characteristic radiation depending on the material of the anti-cathode of the tube. This typical line spectrum originates from purely atomic sources, the lines occurring in series such as the short-wave K series, an L series of longer wave-length, and a long-wave M series. A remarkable feature of these spectra is the fact that a definite line of any of these series shows, for successive elements, a regular advance towards the shorter wave-lengths, with the atomic number of the element; and since, according to modern views, the atomic number of the element is identical with the nuclear charge, we conclude that Röntgen spectra must originate in or near the nucleus. The discovery of the relation between the Röntgen spectra of an element and its atomic number was due to Moseley,[1] whose epoch-making discovery went so far towards an understanding of atomic constitution, and exerted so profound an influence on our knowledge of the chemical elements. Moseley showed that the strongest line in the K series was given by

$$\nu = \mathrm{R}(\mathrm{N} - a)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \quad . \quad . \quad . \quad . \quad 203$$

and similarly the strongest line in the L series by

$$\nu = \mathrm{R}(\mathrm{N} - b)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \quad . \quad . \quad . \quad . \quad 204$$

where N is the atomic number, R the Rydberg constant and a and b two numerical constants. The striking similarity of these relations to Bohr's formula for the optical series for hydrogen leads us to seek an interpretation of the Röntgen spectral series through Bohr's atomic model, and suggests that these spectra should be regarded as the last step of the process whereby the neutral atom is built up by the capture and binding of electrons to the nucleus. Considering the K series as connected with the innermost quantum ring, the series emission will be due to an addition of energy removing an electron to infinity. Denoting the initial and final energies of the atom by W_0 and W_K respectively, the energy provided will be $\mathrm{W}_\mathrm{K} - \mathrm{W}_0$. Hence every energy condition for which $h\nu$ is greater than $\mathrm{W}_\mathrm{K} - \mathrm{W}_0$ will effect the removal of an electron. Then at the point $\nu_\mathrm{K} = \mathrm{W}_\mathrm{K} - \mathrm{W}_0 / h$ an increase in absorption takes place, and from $\nu = \nu_\mathrm{K}$ (the edge of the absorption band) an absorption band extends towards the higher frequencies. If now the electron

[1] *Phil. Mag.* 1913 [vi], **26**, 1024; 1914 [vi], **27**, 703.

falls from the L ring into the K ring, then the first line Kα of the series is emitted; if it falls from the M or N ring, lines K_β or K_γ are emitted; or again if the L ring is ionized and the electron falls from the M to the L ring, the line Lα is emitted.

An ejected K electron cannot be caught on an L, M or N ring, these being already occupied; it may however be caught on an unoccupied orbit outside these, giving a line for which $h\nu$ is equal to the energy difference of the two orbits.

Sommerfeld explained the fine structure of the lines by relativity considerations, the relativity effect being much greater for Röntgen spectra than for optical spectra, since in the former case the electron approaches the nucleus more closely. Difficulties of arrangement make it improbable that the electrons are in plane rings, but rather in spatially symmetrical figures. This however and many other allied details are undecided and await further investigation.[1]

[1] For recent advances on the theory of electron grouping, see Main Smith, *Journ. Chem. Ind.*, 1925, **44**, 944; and Stonor, *Phil. Mag.* 1924, **48**, 719. See also a summary of recent lectures by Sommerfeld. *Nature*, 1926, **117**, 793.

XI

THE CORRESPONDENCE PRINCIPLE AND BOHR'S INTERPRETATION OF THE ELEMENTS

The Selection and Correspondence Principle.—The positions of the spectral lines, depending on their frequency, has been defined by Bohr's theory ; a further principle has been developed to supply information concerning the form of vibration which defines their intensity and polarization. It is also necessary to investigate whether electron jumps from any quantum orbit to any other are permissible, or whether the jumps must be limited in any way. Rubinowicz[1] worked out, from the law of conservation of moment of momentum, a principle of selection according to which, in the case of atoms of the hydrogen type, the azimuthal quantum number n can alter only by 0 or $+1$ or -1 when emission takes place. In the first case the light radiated is linearly polarized, and in the other two cases circularly polarized. For the more complicated types of atom, if the whole moment of momentum of the system is put equal to $nh/2\pi$, changes in the number n are limited in exactly the same manner.

A much more extensive and useful principle has been developed by Bohr,[2] who traced a connection between the occurrence of transitions between stationary states and the harmonic components into which the motion of the atom can be resolved, and which, according to the classical theory, determines the characteristics of the emitted radiation. It is assumed that every transition between two stationary states can be co-ordinated with the corresponding harmonic vibration component, so that the probability of occurrence of the transition is dependent on the amplitude of the vibration. This is Bohr's Correspondence Principle, so called because there is a certain correspondence between the quantum and classical theories under definite limited conditions. The principle is of the utmost importance in the further development of quantum mechanics, not only by reason of its wide utility, but also inasmuch as it appears to be a step towards a co-ordination of classical and quantum dynamics. The classical theory assists and guides a quantum interpretation

[1] *Phys. Zeitschr.* 1918, **19**, 441.

[2] N. Bohr, "On the Quantum Theory of Line-spectra."

of such problems in particular as the polarization and intensity of the emitted radiation, apart from the frequency alone. A compound oscillation is analysed into simple harmonic constituents by Fourier's method, in which such periodic phenomena are represented mathematically by the sum of a number of terms forming a Fourier's series, each term representing a simple harmonic oscillation of the phenomenon under consideration.

Bohr sets up a correspondence between the simple harmonic terms of the classical Fourier's series on the one hand, and the quantum jumps on the other hand. The data concerning polarization and intensity, afforded by the classical theory, are assumed to be approximately true for the corresponding line actually present in the emitted radiation, the agreement being most satisfactory for high quantum numbers and low frequencies. It must be emphasized that the frequencies of the radiation are *not* the frequencies of the harmonic components of the periodic motion. The state of polarization of the emitted radiation is determined by the direction of the linear vibration which constitutes the corresponding mechanical constituent in the orbital movement. In the limiting case of systems possessing a very large number of energy quanta, the spectra predicted on classical and quantum grounds become identical as regards frequency; that is, for high quantum numbers the quantum theory passes over into the classical theory. Although derived from an application for high quantum numbers, Bohr extends his principle, and assumes its applicability for all quantum numbers. If in the classical analysis of a harmonic vibration a periodic term is missing, the correspondence principle leads to the view that radiations of frequencies not represented in the harmonic analysis are of zero intensity, due to the fact that the corresponding electronic transition does not take place.

The Stark Effect. We have seen that the variation in mass of the electron with its speed, and the consequent deviation from true elliptic motion, are intimately connected with the fact that the spectral lines exhibit a fine structure, and consist of groups of lines very close together. Much greater effects are produced by the perturbing action of external forces such as an electrostatic or magnetic field. It was discovered experimentally by Stark in 1914 that a strong external electric field causes the hydrogen spectral lines to split up into a number of lines, the extent of separation being proportional to the intensity of the electric field, and of a much higher order than the fine structure separation previously discussed. The phenomenon has received

satisfactory theoretical explanation by the work of Epstein,[1] and can be clearly treated by Bohr's theory of stationary states supplemented by the correspondence principle. The periodic motion of the perturbed hydrogen atom and the energy of its corresponding stationary states are specified in accordance with Bohr's theory, while the effect of the external agency on the decomposition of the motion into harmonic oscillations is investigated with the help of the correspondence principle. In this way the position and number of components of the resolved lines are given in complete agreement with experimental results, while the polarization observed also receives explanation. The relative intensity of the components has also recently been treated theoretically by Kramers.

The Zeeman Effect.—Zeeman in 1896 discovered that under the influence of a powerful magnetic field, spectral lines of the simpler type were resolved into doublets and triplets, the effect in general being much simpler than for an electric field. A complete and satisfactory analysis of this effect was developed by Lorentz on the classical theory. Exactly as for the Stark effect, Bohr's theory is applicable for the Zeeman effect, while the problem has been treated on somewhat different lines by Debye [2] and Sommerfeld,[3] who have arrived at results completely in agreement with those of the classical theory for the simple elements hydrogen and helium.

The action of a magnetic field on spectra of a more complicated nature, for which the model of the emitting system is more complex (e.g. the sodium lines), gives rise to an anomalous Zeeman effect containing lines not completely predicted and explained by the extension of Bohr's theory. This however has been explained on a classical basis for the sodium D lines by Voigt,[4] while more recently the problem has been further treated on a quantum basis by Sommerfeld [5] and Debye, who have shown that only certain orientations of the atom relative to the magnetic field were allowable. The difficulty of the anomalous effect is at once overcome by the application of the correspondence principle, which explains the non-occurrence of certain transitions and the observed polarization.

The limited atomic orientations have been confirmed by the beautiful researches of Stern and Gerlach. These investigators

[1] *Ann. Physik*, 1916 [iv], **50**, 489.
[2] *Phys. Zeitsch.* 1916, **17**, 507.
[3] *Ibid.* 491.
[4] *Ann. Physik*, 1913 [iv], **41**, 403; 1913 [iv], **42**, 210.
[5] *Zeitsch. Phys.* 1922, **8**, 257.

subjected silver atoms, obtained by boiling silver in an electric furnace, to the influence of a non-homogenous magnetic field, and found that instead of the atoms pointing arbitrarily in all directions, they were all pointing towards or away from the magnetic field.

Bohr's Interpretation of the Chemical Elements.[1]—The ideas which have been outlined on the origin of spectra have been utilized by Bohr, in conjunction with the correspondence principle, for an interpretation of the natural system of chemical elements as illustrated by the periodic table. The basis of the theory is a consideration of the manner in which an atom can be imagined to be built up by successive capture and binding of electrons, one by one, in the field of force surrounding the nucleus. Although a striking similarity has been pointed out between the X-ray spectra and the hydrogen spectrum, an important difference must be emphasized. For while the emission of the hydrogen spectrum may be assumed to be connected with the binding of an electron by the atom, there are clear indications that the X-ray spectra are connected with a process of reorganization of electronic arrangement after a disturbance within the atom, due to some external agency. This indicates the dependence of X-ray spectra upon both the interaction between an electron and the nucleus, and the manner of arrangement of the electrons in the atom.

Bohr developed a modified arrangement of a form of the periodic table proposed by J. Thomsen, and tabulated a scheme giving the probable structure of each element from a consideration of its atomic number, or number of electrons in the neutral atom, and showing the number of electrons in orbits corresponding to the values of the principal and subordinate quantum numbers. In this way, as the electrons are bound in successive quantum orbits, closed configurations are reached at intervals corresponding to the inert gases. A similarity is therefore shown to features of the scheme suggested in 1904 by J. J. Thomson, of building up the elements by groupings of electrons in rings about the nucleus. This scheme was developed by Kossel [2] in 1916, in the light of advancing knowledge of X-ray spectra.[3] Although Thomson's ring grouping accounted for the orders of magnitude of atomic dimensions, as well as the stability of the atoms in terms of their electron groups, it did not afford a detailed explanation of the characteristic properties of

[1] Bohr, *Theory of Spectra and Atomic Constitution* (Camb. Univ. Press).

[2] *Ber. deutsch. physikal. Ges.* **1916, 18,** 339.

[3] Moseley's work has largely been developed by Prof. Siegbahn.

the elements. Moseley's laws of X-ray spectra and Sommerfeld's theory of the fine structure of spectral lines suggested the idea of connecting the electron grouping with a classification of electron orbits according to increasing quantum numbers, an idea which was still further extended by the study of the binding of electrons as interpreted by optical spectra and their treatment by the correspondence principle. Bohr applies the correspondence principle to the motion of the electron last captured, and the occurrence of transitions between the stationary states corresponding to various stages of the binding process, and rejects, from among all the quantum permissible processes, those which are not in agreement with the correspondence principle.

The orbits of an atom containing several electrons will in general be of a complicated character. Since the field of force about the nucleus is of a symmetrical nature the motion of each electron can be approximately described as a plane periodic motion on which is superimposed a uniform rotation in the plane of the orbit. The orbit of each electron will therefore be doubly periodic and fixed by two quantum numbers. The periodic variation with the atomic number, of many properties of the elements, is connected with the fact that in the last stages of the binding process, the orbit of the last electron captured penetrates into the inner region of the previously bound electrons, and consists of a series of loops each of which is turned through a small angle relative to the preceding one. On account of this penetration, the strength with which such an electron is bound will be much greater than for an electron having the same quantum orbit and moving in the hydrogen atom. The influence of this penetration is an essential cause of the periodicity in various properties of the elements. We also find that the increase in the principal quantum number explains certain deviations from periodicity shown in the table. In Fig. 6 the elements are arranged in columns representing periods, and in the order of their atomic number ; the lines connect, in successive periods, elements showing chemical and physical similarities. In the following discussion let us denote quantum orbits by n_k where n is the principal quantum number and k the subordinate quantum number.

The group of electrons in 2-quantum orbits is entirely completed at the end of the second period. Period 3 shows the development of the 3-quantum orbits, which is only partially completed at the end of that period ; in the 4th period it undergoes a further stage of development which is represented by a group of elements (in a rectangular enclosure) from scandium to

nickel. For potassium, which begins the 4th period, the principal quantum number of the last electron bound is larger, in the normal state of the atom, than in one of the earlier stages of the binding process. The normal state here corresponds to a 4_1 orbit, which owing to penetration is stronger than a 4-quantum orbit in the hydrogen atom, or a 3_3 circular orbit exhibiting no penetration. The binding of the 19th electron for calcium in a 4_1 orbit is little stronger than in 3_3 orbits, while starting with

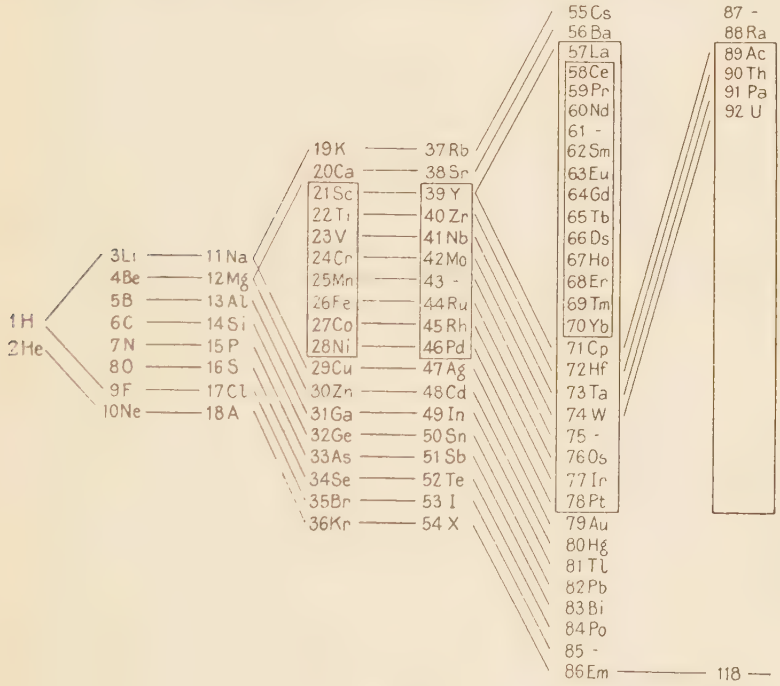

FIG. 6.

scandium the 3_3 orbit represents the normal orbit stronger than a 4_1 orbit. At this stage the 4-quantum orbit development ceases until the completion of the 3-quantum group in nickel. Similarly in the 5th period a group of elements from yttrium to palladium represents the completion of the normal 4_3 orbits. In the 6th period, not only is there a development of the 5- and 6-quantum orbits, but in addition a final completion of the 4-quantum group, starting with the entrance of the 4_4 electron orbits into the normal atomic state. This development of an inner electron group affords

a beautiful and natural explanation of the rare-earth family of elements, which had presented so much difficulty in the earlier formulations of a periodic table. A similar argument applied to the 7th period leads us to expect further stages in the development of 5- and 6-quantum orbits. In the 7th period, however, there are only a few elements known, while the instability of the nucleus with large charges provides an explanation of the radioactive elements found in this region.

Since the publication of Bohr's work which we have been discussing, a new element of atomic number 72 has been discovered by Coster and Hevesy,[1] and takes its place in the table of elements, in agreement with theoretical requirements.

Einstein's Deduction of Planck's Radiation Law from a generalized Bohr Model.[2]—It will have been noticed that the deductions of Planck's Law which have been considered are not completely independent of classical electrodynamics. An attempt has been made by Einstein to avoid the introduction of classical laws into the interaction of oscillators and radiation, and for this purpose he has replaced Planck's linear oscillator by a generalized Bohr model, which possesses the essential quantum feature of being able to assume definite stable states with definite energy contents, and considers the equilibrium between black-body radiation and the Bohr model.

Denote conditions of higher and lower energy of the atom by E_2 and E_1 respectively, and denote the number of atoms momentarily in the corresponding energy states by N_2 and N_1. Einstein assumes that the frequencies of emissions, or transitions involving loss of energy, between two states, follow the law of radioactive disintegration, i.e. the number of transitions in time dt is given by $N_2 dt$. A different law, however, must regulate the processes called into existence by the effect of external radiation, under the influence of which the atom may either pass from the state E_1 to E_2 (absorption); or from E_2 to E_1 (negative absorption), or loss of energy through the action of the radiation. In each case the rates of transition are proportional to K'_ν the intensity of the external radiation, and in the first case the rate is proportional to $N_1 dt K_\nu$, in the second case to $N_2 dt K_\nu$.

N_1 and N_2 are known from the statistical probability of the states to be proportional to $p_1 e^{-E_1/KT}$ and $p_2 e^{-E_2/KT}$ respectively,

[1] Letters to *Nature*, 1923, **111**, 79, 182, 252 and 462. Still more recently the discovery of elements of atomic numbers 43, 61 and 75 has been announced.

[2] *Ber. deutsch. physikal. Ges.* 1916, **18**, 318; *Phys. Zeitsch.* 1917, **18**, 121.

where p_1 and p_2 are factors denoting the intrinsic probability of the state in question.

Hence we have for equilibrium

$$N_2 dt + N_2 dt K_\nu = N_1 dt K_\nu \quad . \quad . \quad . \quad . \quad 205$$

also

$$\frac{N_2}{N_1} = \frac{p_1 e^{-E_2/KT}}{p_2 e^{-E_1/KT}} = \frac{p_2}{p_1} e^{-(E_2 - E_1)/KT} \quad . \quad . \quad . \quad 206$$

Combining these equations we finally obtain

$$K_\nu = \frac{A}{e^{\frac{E_2 - E_1}{KT}} - 1} \quad . \quad . \quad . \quad . \quad . \quad 207$$

where A is a constant. From Wien's displacement law it follows that

$$A = a\nu^3$$
$$E_2 - E_1 = h\nu$$

where a and h are constants, the latter equation being Bohr's frequency condition. Planck's radiation law has thus been arrived at in a simple manner and with a minimum of general assumptions.

XII

CONCLUSION

In the preceding pages an attempt has been made to present some account of one of the outstanding theories of contemporary physics. Starting from a restricted sphere, the growth and ramifications of the Quantum Theory cannot be regarded as less remarkable than the success which has attended its application. Although it has assisted so largely to systematize and unify our knowledge of physical phenomena, we appear to be very little nearer an understanding of the inner mechanism of the problems with which it deals. The difficulty is to formulate a satisfactory physical basis for the theory, and to present a mental picture of the fundamental processes concerned; a discontinuity in nature. Two basic problems still remain unsolved: the formulation of a fully generalized system of quantum mechanics, and the establishment of the precise relation of the modern theory to the older classical theory. The difficulties of a complete reconciliation of the two theories seem insuperable, so that at present we are in the not altogether satisfactory position of having to retain the best features of the classical theory and adapt them to quantum requirements. That radiant energy and light must exist under all conditions in finite quanta is an unacceptable view, and has been broken down by the criticisms of Lorentz as well as by the experimental work of Taylor,[1] who showed that interference phenomena took place when light was so feeble that two or more quanta could not possibly exist at the same place simultaneously. It has been emphasized in these pages that we must adopt the more conservative view, in keeping with Planck, of confining the application of quanta to the interaction between matter and energy.

At the present time active progress is being made in a deeper study of spectra. A Quantum Theory of X-ray scattering has been proposed by Compton,[2] who discovered that the scattering of homogenous X-rays is accompanied by a change of wave-length in the scattered radiation depending on the direction of

[1] *Proc. Camb. Phil. Soc.* 1909, **15**, 114.

[2] *Bull. Nat. Research Council*, 1922, No. 20, p. 19; *Nature*, 1923, **112**, 435; 1924, **114**, 627.

observation. This can be explained on the light quantum hypothesis of taking account of the conservation of momentum and energy. Barkla [1] criticizes Compton's theory, and refers to the so-called J transformation [2] which is associated with a discontinuity in the absorption by a given substance of X-radiations. While Compton considers the change in wave-length to take place when the ray is scattered, Barkla is of opinion that the J transformation is not in the process of scattering but in the subsequent transmission of scattered radiation through the radiating substance and through absorbers ; he also inclines to Thomson's classical theory of scattering. Dispersion has been discussed by Kramers [3] in the light of the correspondence principle and developed by Kramers and Heisenberg.[4]

An interesting view is advanced by de Broglie,[5] who assumes the existence of a periodic phenomenon which is connected with every isolated portion of energy, electrons, protons, matter and quanta, and offers suggestive lines for further advance.

The various difficulties associated with quantum dynamics have been recently reviewed by Heisenberg, who in a most important paper [6] has suggested a scheme of quantum mechanics in extension of the correspondence principle, and which it is hoped will prove of definite value in overcoming a number of difficulties which have developed in the study of the finer details of spectra.

A new epoch in Quantum dynamics appears to have been opened by the recent system of mechanics developed by Heisenberg and others, by introducing matrix analysis. This is already being referred to as the New Quantum Theory, and some account of it is given in an article by Flint.[7] Attention must also be directed to recent work on the theory of the spinning electron.[8] The co-ordination and application of these lines of advance will be worthy of close attention.

[1] *Nature*, 1923, **112**, 723 ; 1924, **114**, 753.
[2] Bakerian Lecture, *Phil. Trans.* 1917, **217**A, 315 ; *Nature*, 1925, **115**, 604.
[3] *Nature*, 1924, **113**, 673 ; **114**, 310.
[4] *Zeitsch. Phys.* 1925, **31**, 681.
[5] *Ann. Physique*, 1925, **3**, 22 ; *Nature*, 1923, **112**, 540.
[6] *Zeitsch. Phys.* 1925, **33**, 879.
[7] *Science Progress*, July, 1926.
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